TEMPORAL VARIABILITY OF DIN, CHLOROPHYLL, AND DOC IN FLORIDA BAY FOLLOWING HURRICANE IRMA

Timothy Joseph Wahl

A thesis submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Marine Sciences.

Chapel Hill
2019

Approved by:

Christopher S. Martens

Michael F. Piehler

Adrian Marchetti

ABSTRACT

Timothy Joseph Wahl: Temporal Variability of DIN, Chlorophyll, and DOC in Florida Bay following Hurricane Irma
(Under the direction of Christopher S, Martens)

In September 2017 Hurricane Irma passed over the Florida Keys causing extreme damage to aquatic environments and populated land areas. At some locations, the hurricane caused water to recede over 100 meters from the Florida bayside shoreline, resulting in catastrophic damage to nearshore benthic communities including sponges, whose total biomass decreased by approximately 95 ± 5% in one middle Keys embayment site. A post-Irma time-series study of water quality parameters was conducted featuring monthly sampling from Middle Keys embayments, nearshore waters, and a western Bay basin. This study focused on determination of the impacts of episodic storm events on temporal variability in dissolved inorganic nitrogen concentration. The monthly whole water samples were filtered for chlorophyll-a measurements and then analyzed for nitrate/nitrite, ammonium, and dissolved organic carbon. The results revealed drastic, systematic changes in water quality following Hurricane Irma including spiked DIN concentrations following sediment resuspension and release of NH_4^+-enriched pore-waters into the overlying water. However, after four months, concentrations returned to pre-Irma levels according to a previous multi-year survey.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF ABBREVIATIONS

BKB: Back Key Basin region (Briceño and Boyer 2013)

Chl-a: Chlorophyll-a

DIN: Dissolved Inorganic Nitrogen ([NO_x^-] + [NH_4^+])

DOC: Dissolved Organic Carbon

FWC-M: Florida Fish and Wildlife Conservation Commission based in Marathon, FL

LGW: Lab Grade Water

NH_4^+: Ammonium Concentration

NO_x^-: Nitrate and Nitrate Concentrations calculated together ([NO_3^-] + [NO_2^-])

SD: Standard Deviation

SERC: Southeast Environmental Research Center, Florida International University

SFB: Southern Florida Bay (Briceño and Boyer 2010)

Site: Area in which the sampling station exists

Station: Point at which monthly nutrient collection samples were taken

TOC: Total Organic Carbon

WFB: Western Florida Bay (Briceño and Boyer 2010)

CHAPTER 1: TEMPORAL VARIABILITY OF DIN, CHLORPHYLL, AND DOC IN FLRODIA BAY FOLLOWING HURRICANE IRMA

Introduction

Florida Bay is located between the Florida Keys and the southern tip of mainland Florida. This Bay is shallow, average depth less than three meters, and historically oligotrophic (Fourqurean et al. 1992). Florida Bay can be sectioned into four regions defined by their differing physical parameters including salinity and mixing (Nuttle et al. 2000) and can be separated further by chemical parameters (Fig. 1) (Briceño and Boyer 2010, 2013) and sediment types (Prager and Halley 1997). Primary productivity, largely conducted by seagrasses, is generally limited in the southern, eastern, and east-central regions by phosphorous (Boyer et al. 1997, Fourqurean and Robblee 1999, Briceño and Boyer 2010). Conversely, nitrogen is generally limiting in the western and central regions due to the exposure from the open Gulf of Mexico to the west (Fourqurean et al. 1993, Hunt and Nuttle 2007). Under natural conditions in Florida Bay, seagrasses dominate as the main primary producer at locations where surface water nutrient concentrations are low, as seagrass root structure can penetrate into nutrient-rich sediment porewaters (Fourqurean et al. 1992, Hall et al. 1999). If water column nutrients are increased, oligotrophic conditions are not met, and phytoplankton biomass may increase including sporadic occurrences of large-scale blooms of cyanobacteria (*Synechococcus*) or diatoms (Philips et al. 1999, Lindell et al. 2005).

Although phytoplankton biomass has remained generally low throughout the Bay because of the oligotrophic conditions, documented bloom events have occurred more frequently in recent decades, creating large-scale impacts on Florida Bay water quality (Boyer et al. 1999, Boyer et al. 2009, Briceño and Boyer 2010). Phytoplankton blooms which result from either natural or anthropogenic impacts are a detriment to benthic as well as pelagic communities in Florida Bay, causing long-term alterations in regions hit with large-scale events. Changes in Florida Bay ecosystems have generated greater concern after a major seagrass die-off occurred between 1987 to 1991. The seagrass die-off was caused by a multiyear drought that increased salinity up to 70 psu, (Fourqurean and Robblee 1999, Zieman et al. 1999) and elevated nutrient concentrations throughout the Bay which lead to regional water quality degradation (Lapointe and Barile 2004). After the seagrass loss, water column turbidity increased due to reduced abundance of seagrass root systems controlling sediment resuspension (Hall et al. 1999) and decreased baffling of currents by the seagrass leaves. Diminished seagrass populations allowed for the nutrient pools in the sediment to accumulate due to declined seagrass root uptake, as well as less drawn down of water column nutrients by seagrass leaves (Fourqurean et al. 1992). Beginning in 1991, yearly cyanobacteria blooms developed in the north Central Bay leading to sponge population decline. The underlying cause for these blooms was suggested to result from the loss of seagrass across the Bay (Butler et al. 1995). One of these sustained cyanobacteria blooms occurred in Western Florida Bay during Fall 2013 through Spring 2014, which lead to a large sponge biomass loss at station MB1, one of our field stations in Mystery Basin (Fig. 2a; 24°56’30.42”N 80°49’31.80”W) (Hoer 2015, Sharp et al. FWC-M). The bloom appears to have been initiated in the upper central Bay, but was sustained in the basin due to long basin water residence times of up to two weeks (Rok et al. In Prep) allowing the blooms conditions to continue and leading to a 99% biomass loss of sponges (Hoer 2015). This event created a feedback loop as decaying sponge biomass provided a source of remineralized nutrients enhancing the phytoplankton bloom and creating an environment where the bloom could persist (Hoer 2015).

Seagrass loss is not the only contributor to phytoplankton blooms in Florida Bay. Disturbances from hurricanes are known to bring about significant bloom (Briceño and Boyer 2010, Hunt and Nuttle 2007). Eastern Florida Bay had experienced very few phytoplankton blooms until 2005 when a busy hurricane season (Katrina, Rita, and Wilma) caused a cyanobacteria bloom in the region (Rudnick et al. 2007). The bloom occurred due to pulses of nutrient loading coming from runoff of the Everglades and precautionary flood discharges from canals into Eastern Florida Bay (Rudnick et al. 2007, Boyer et al. 2009). The bloom was sustained in the region for several months due to long water residence times and efficient nutrient retention (Rudnick et al. 2007). In Fall 1998, Hurricane Georges passed over the west potion of Florida Bay, uprooting and reducing seagrass cover at four of nine field stations at Johnson Key Basin; similarly, a significant reduction of seagrass was also reported after Hurricane Irene in Fall 1999 (Hunt and Nuttle 2007, Durako et al. 2002). As the seagrass was removed from the sediment, it began to decompose in the water column increasing readily available, labile organic matter. The increased reactive organic matter along with increased nutrients, caused by sediment resuspension from the hurricanes, resulted in the phytoplankton blooms (Hunt and Nuttle 2007, Briceño and Boyer 2010). Hurricanes have previously been shown to cause increased nutrient loading in estuarine systems along the Eastern and Gulf coasts. In North Carolina, U.S.A., freshwater discharge into the Neuse River Estuary – Pamlico Sound (NRE-PS) from large storms has been shown to be critical in understanding nutrient dynamics for coastal ecosystems. Hurricanes Dennis, Floyd, and Irene were responsible for greater than 90% of the annual Total Phosphorous (TP) and Soluble Reactive Phosphate (SRP) loading, and about 50% of annual Dissolved Inorganic Nitrogen (DIN) loading (Paerl 2018). This comparison between the NRE-PS region and Florida Bay appears appropriate when analyzing the discharge of freshwater from the Everglades, which was one of the causes of the 2005 phytoplankton bloom in Eastern Florida Bay. In addition, hurricanes increase the loading of terrigenous DOC during storm flow (Paerl 2018) which could cause increases in microbial growth as well as oxygen consumption creating anoxic bottom waters resulting in benthic biomass loss. These episodic events altered water column nutrients and benthic community structure, threatening the Bay and the Florida Keys as a whole from economic, social, and environmental perspectives.

Hurricane Irma:

Hurricane Irma crossed over the Middle Florida Keys on September 10, 2017 as a category 4 storm with winds up to 130 mph. As Hurricane Irma approached the Keys island chain from the south, waters receded approximately 100m from bayside the shoreline along some parts of the Middle Keys (W. Sharp, personal communication). As a result of the receding waters, subtidal benthic organisms including sponge and seagrass populations were subaerially exposed, and as the hurricane moved overland, were apparently physically ripped from the newly exposed sediment. Pre-and-post sponge surveys conducted by FWC-M scientists at the Burnt Point site (BP, Fig. 2b) (24°45'24.60"N 80°58'55.00"W) used in the present study, revealed the loss of total sponge biomass at approximately 95 ± 5% (Bollinger et al. 2018).

Sponges have multiple vital roles in Florida Bay as they serve as habitats for both microbial and macrobenthic organisms (Southwell et al. 2008, Butler et al. 1995), create plankton grazing pressure (Peterson et al. 2002, 2006), and recycle dissolved inorganic nitrogen

(DIN) and other nutrients to the water column during respiration of labile organic matter (e.g. Corredor 1988, Southwell et al. 2008a, Hoer et al. 2018). Sponges are known sources of all chemical species of DIN through production and chemical transformations by hosted microbial associates. The form of DIN (NH_4^+ or NO_3^-) that is excreted from various sponge species depends upon the speciation and quantity of the microbial community associated with each sponge species (e.g. Southwell et al 2008b, Jimenez and Robes 2007). Low microbial abundance (LMA, Hentschel et al. 2006) sponges generally recycle organic N as ammonium (NH_4^+); conversely, high microbial sponges (HMA) largely produced nitrate and nitrite (NO_x^-) (Southwell et al 2008b; Hoer et al. 2018). Our MB1 site experienced a dramatic drop (48 ± 24%) in recycled DIN source after the 99% sponge biomass loss which was caused by the cyanobacteria bloom in Fall 2013 (Hoer 2015). The impact of this catastrophic sponge removal on recycled DIN inputs to the MB1 water column suggested that sponge biomass losses after Hurricane Irma at BP and the nearshore Middle Keys should be included in the study to compare the impacts of these episodic events on water column DIN concentrations.

More research questions developed as new discoveries were made after the start of this study in Fall 2017. The initial goal was to quantify the effect of high sponge biomass loss on DIN by measuring changes in its concentration on a monthly timescale at the middle Keys embayment station BP. A comparison was drawn to similar Mystery Basin data from the 2013-2014 bloom study (Hoer 2015), in order to seek relationships between results from a central Bay basin location and a nearshore embayment along the Keys island chain. While completing DIN measurements in Florida Bay, a wind event caused DIN concentrations to increase at our field sites creating a new hypothesis about sediment resuspension and the release of stored NH_4^+ could be a major source of new DIN into the system. This hypothesis needs to be explored further across the variety of sediment types that have been documented in Florida Bay (e.g. Prager and Halley 1997). As DIN concentrations returned to a long-term data set baseline, spatial differences in DOC concentrations data between nearshore Key and interior locations became more apparent and were also included in the study. Dramatic differences in DOC values observed after phytoplankton blooms and concentration differences between interior Bay locations versus stations close to the Keys island chain raised interest in searching for sources of additional DOC. All of these topics were explored during this study.

Methods

Site Selection:

For this experiment, 12 stations (Fig. 2, Appendix 2) across three sites were chosen based on work conducted between 2012 and 2015 by colleagues at UNC and FWC-M. To keep the representation of the data concise, I have chosen three stations that are representative of the sites (A3) to present in this study, MB1, BP, and J01 (24°49'54.30"N 80°48'44.82"W). MB1 is the central location of our Mystery Basin site, located in West Florida Bay (WFB). Florida Bay contains small basins which are created through shoaling carbonate sediments, causing the basins to have lowered physical exchange. Water exchanges with MB through the sill in the North-Northwest (Hoer 2015, Rok et al. 2019). The water inside Mystery Basin is heavily influenced by the output of the Everglades. Mystery Basin represents the central portion of Florida Bay which is comprised of basins with a similar submerged sill. Burnt Point is located in the Back Key Basin (BKB) region and represents nearshore embayments, a common feature along the Keys. Due to the proximity to land, embayments could be more influenced by runoff from the Keys. In addition, the BP field site underwent a sponge biomass loss of approximately 95 ± 5% during Hurricane Irma (Bollinger et al. 2018). The last field site is Long Key which is a nearshore location, but not an embayment like BP. The J01 station from Long Key site is closer to the shoreline but is representative of the full site. Together, the Long Key and BP sites, are representative of the range of nearshore environments along the southern portion of Florida Bay.

Sample Preparation:

From each of the stations whole water samples utilized for all measurements were collected in duplicate, 10 cm below the surface, on a monthly basis beginning on October 31, 2017. Samples collected by FWC-M personnel on most dates could only be provided in frozen, unfiltered form due to limited availability of boating operations and sample handling personnel at their laboratory following Hurricane Irma. The whole water samples were frozen with dry ice and shipped to UNC-Chapel Hill for completion of the analyses. The UNC team worked out of the FWC-M laboratory and collected water samples on Dec 5, Dec 11, April 3, April 9, and Sept 27. Samples from these four dates were filtered prior to freezing and shipping to UNC. Cell lysis undoubtedly occurred in the frozen samples collected by FWC-M personnel and shipped unfiltered to UNC, thereby suggesting that their Chl-a measurements represent minimum concentration values.

All samples were vacuumed filtered through a 47 mm Whatman GF/F. The filters were placed in combusted foil for chlorophyll-a (Chl-a) measurements, and then stored in a -20°C freezer prior to other analyses. Chl-a measurements from our study can be used as an indicator for minimum algal biomass, but cannot be used as a definitive phytoplankton measurement due to probable cell lysis in the unfiltered frozen samples as well as variability in cellular chlorophyll content (Boyer et al. 2009). However, careful comparisons of Chl-a, DIN, and DOC results (Appendix 5) show that DIN and DOC measurements made on unfiltered samples were not significantly altered. In particular, lowest DIN values were always seen in frozen unfiltered samples collected during known bloom conditions indicating that DIN release due to cell lysis is not significant. In addition, the DIN concentrations are within error of baseline data from a multiyear study during non-event periods. Chl-a concentrations in both sets of samples were lower than baseline data from a previous multiyear study, however, analytical errors for each set were similar (Appendix 1).

Amber tinted HDPE bottles were used for NH4+ analyses in order to limit light exposure to the samples, and borosilicate vials used for NOx- and DOC analyses were acid washed in a 0.1M HCl bath for at least twelve hours and rinsed with 18.2 MΩ water (LGW). The borosilicate vials were combusted at 450oC for at least six hours. The amber tinted bottles had o-phthaladehyde (OPA) working reagent added for 24 hours to react any trace amount of NH_4^+ and rinsed again with LGW prior to the filtrate added.

For analysis, 20 mL aliquot of filtrate was sectioned into two HDPE bottles for duplicate NH_4^+ analysis, 20 mL in two borosilicate scintillation vials for DOC analysis, and 20 mL in two borosilicate scintillation vials for NO_x^- analysis. For the NH_4^+ samples, 5 mL OPA reagent (Holmes et al. 1999) was added to the amber HDPE bottle to react with the NH_4^+ for analysis. For the DOC samples, 0.1 mL of 50% phosphoric acid was added to the vials to acidify the sample to a pH 2 solution, in order to remove DIC by the instrument. The NH_4^+ analyses were conducted the same day as filtration, DOC samples were stored in a 4.0°C refrigerator, and the NO_x^- samples were stored in a -20°C freezer.

Sample Analysis:

The method described in Holmes et al. (1999) was used to measure NH_4^+ concentrations in all samples. After the sample reacted with the 5 mL OPA reagent for 2.5 hours at room temperature, they were analyzed in a Turner Design TD-700 laboratory fluorometer with a near

UV lamp (310-390 nM). Calibration standards were prepared the day of analysis from a SPEXCertiPrep 1000 µg/mL stock solution. For NO_x^- analysis, discrete samples were measured using the Spectrophotometric Elemental Analysis System (SEAS) configured for benchtop applications (Adornato et al. 2005). The SEAS methodology utilizes the Griess reaction to determine concentrations of NO_x^- (Adornato et al. 2007). The SEAS technology has a detection limit of 25 nM. Standards for NO_x^- measurements were prepared daily using SPEXCertiPrep 1000 µg/mL. The DOC analyses were conducted on a Shimadzu TOC-L/TNM-L organic carbon and total nitrogen analyzer. The sample was combusted and analyzed using non-dispersive infrared spectroscopy (NDIR). DOC values obtained by this method are non-purgeable organic carbons (NPOC) due to a purging step via sparging during analysis to remove DIC from the sample. The difference between NPOC and DOC are assumed to be negligible due to low concentration of volatile organics in Florida Bay. Lastly, phytoplankton abundance was measured by the proxy of chlorophyll-a using the acidified fluorometry method (Yentsch and Menzel 1963). A Turner Design 10-AU Fluorometer was used for analysis with a standard curve calibrated using a spinach chl-a extract. The values of phytoplankton are reported in µg/L and all nutrients are reported in µM, error reported in this study is representative of one sigma values.

Shake and Core Experiments:

Qualitative shake experiments were performed to mimic how storms resuspend sediment and release stored DIN, impacting nutrient concentrations in particular NH_4^+. Shake experiments were conducted in April and June 2018. To carry out these tests, a 5-sided acrylic cube chamber was placed open face down on the sediment surface of BP. The chamber was brushed along the surface of the sediment back and forth twenty times the length of the cube. This experiment simulated heavy advective motion that could resuspend the sediment. Water was removed from the cube by a 60 mL polypropylene syringe to a volume of 120 mL and stored on ice in an amber HDPE bottle, to eliminate exposure to light. The shake experiment is not easily replicable but gives a good qualitative answer. After significant increases in NH_4^+ concentrations were discovered during shake experiments, a more quantitative core experiment was conducted in June 2018. For the coring experiment, cores were cut at 8.5, 10, and 11.5 cm lengths. A headspace of 6.5 cm was marked on each of the cores leaving 2, 3.5, and 5 cm sediment depths. Sediment was collected to each of those depths in BP, then shaken into the headspace twenty times and poured through a 125 μm mesh filter. These water samples were also vacuum filtered using 47 mm Whatman GF/F. The intent of the core experiment was to gather replicable values of nutrient enrichment within the sediment.

Results and Discussion

Data from monthly samples collected from Oct 2017 through Dec 2018 at all 12 stations (one at BP, two at Long Key, and nine at MB) are reported in Appendix A. On Dec 11, 2017 a sample was not collected from the station at BP due to weather conditions; however, sampling was completed at both the nearby Long Key stations J01 and E02. In this thesis, 3 stations will be focused on, one from each site, that represent temporal trends of the region in order to avoid more complex discussions about physical mixing within each site. The three stations that will be focused on are BP, J 01, and MB1. The general trends of each site across all stations are plotted in Appendix 3. DIN concentrations were calculated for all sites through the addition of NH_4^+ and NO_x^- concentrations. The DIN concentrations of the monthly samples are plotted with relative Chl-a data across the 15-month sampling interval (Fig. 3) at the three representative stations.

Monthly Variability in DIN and Chl-a Concentrations at Three Representative Stations:

Initial data at all twelve stations was collected starting on Oct 31, 2017, 51 days after Hurricane Irma. This was the first chance for FWC-M to help gather the samples for analysis due to personnel issues, repairs, and boat access after the storm. At station MB1, the DIN concentration measured on Oct. 31, 2017 was low, 0.46 µM, while the Chl-a concentration was high, at minimum 8.58 µg/L, a pattern seen previously at our Mystery Basin field site during a massive Synechococcus bloom in 2013-2014 (Hoer 2015). DIN concentrations were slightly elevated at stations J01 and BP, 1.73 and 3.20 µM respectively, compared to MB1 on Oct 31, 2017, however, Chl-a concentrations remained low at both stations compared to MB stations. The elevated DIN could be a result of either post hurricane release of stored DIN in the sediments or from sponge biomass decay following a massive kill associated with Irma. The increased levels of DIN with little to no increased Chl-a concentrations suggest phosphorus limitation of phytoplankton primary production at the BKB sites during the post-hurricane recovery.

At both of the nearshore sites there was a significant decrease in the concentration of DIN by Dec 5, 2017, which was accompanied by a relative rise in Chl-a concentrations, signifying an increase in phytoplankton abundance. The elevated DIN concentration seen at MB1 on Dec 5, 2017 most likely results from the decay of phytoplankton bloom detritus as further indicated by drastic declines in Chl-a concentrations between Oct 31 and Dec 5, 2017.

A wind storm event featuring gusts of up to 15 m/s passed through the Middle Keys on Dec 9, 2017 (NOAA Vaca Key Buoy Station VCAF1). This storm caused massive sediment resuspension, turning the water column “milky” white as often observed in the Bay after persistent high winds. The backscatter data measured by our ADCP current sensor at BP is shown in Fig. 4. The increased backscatter signal is related to sediment resuspension, as backscatter is proportional to particle load in the water column. The DIN pool in the upper five cm of Florida Bay sediments is far greater than that in the overlying water column (Fourqurean et al. 1992, Yarbro and Carlson 1998), therefore, sediment resuspension can release significant quantities of porewater enriched in dissolved NH_4^+. In addition to the porewater release, the resuspended sediment can reintroduce organic matter back into the water column for remineralization (Tengberg et al. 2003). No sample was collected at the BP station on Dec 11, 2017, however, a significant increase in DIN must have also occurred there as well based on backscatter data along with the increased concentration found at nearby J01. The wind storm on Dec 9, 2017, appears to have led to a DIN increase in the water column similar to that found on October 31, 2017, 51 days after Hurricane Irma passed over. It appears that strong storms can significantly increase water column DIN concentrations in shallow Florida Bay as a result of porewater injection and remineralization of the sediment during resuspension at nearshore sites. As shown by our data set, these nutrient concentration increases can occur almost instantaneously when sediments are resuspended during storms.

After enhanced concentrations were found at BP and J01 on Dec 11 2017, DIN and relative Chl-a decreased by over 60% and values remained roughly similar (Fig. 3) until the beginning of spring 2018. Following spring months, the DIN concentrations continuously increased at all three sites (Fig. 3) with the exception of BP on May 23, 2018 when increased relative Chl-a concentrations once again indicated increased phytoplankton growth. As the summer progressed, DIN concentrations increased to a maximum in September and October then precipitously decreased leading into the fall. In central and western Florida Bay, Boyer et al. (1999) previously observed a long-term trend of decreasing DIN in the summer months associated with increasing concentrations of Chl-a. Their results covering the years 1989 – 1998 do not align with our post-Irma data as both DIN and Chl-a were generally higher in the late summer months except during bloom events. If fresh organic matter has been delivered to surficial sediments following storm events, increased temperatures during the summer should allow for greater DIN production and NH_4^+ storage in porewaters resulting from organic matter degradation by the sedimentary microbial community, potentially leading to a larger flux of DIN out of the sediments and its accumulation in the water column in the absence of phytoplankton blooms.

Spatial and Temporal Variability in DOC Concentrations:

DOC concentration values at J01 and BP (Fig. 5) were stable during February through August 2018, averaging 195 ± 46 and 249 ± 48 µM respectively. This narrow range in concentrations could result from the continuing presence of a well-mixed, non-reactive fraction of the total DOC. Temporal variability in DOC concentrations generally appears to follow the same variations in Chl-a concentrations at those stations. Between Dec 2017 and Feb 2018, DOC concentrations decreased by an average 57% at the two stations when Chl-a concentrations remained low. After February 2018, DOC concentrations rose, slightly peaking in the late summer at both sites, following a similar trend as measured Chl-a concentrations. These results suggest that a relatively more reactive component of the total DOC pool is added by primary producers during blooms and then is removed by an unknown uptake process within the month. In the future it would be useful to compare stable isotopic carbon and radiocarbon values between bloom and non-bloom samples in order to help resolve whether the hypothesized "excess DOC" is derived from freshly produced and rapidly decaying algal detritus.

At station MB1, the DOC concentration peaked in October 2017 in conjunction with extremely high Chl-a occurring during a post-Irma bloom. From Dec 2017 through Dec 2018, DOC concentrations averaged 442 ± 60 µM, roughly twice the concentrations found at nearshore stations BP and J01. The peak value measured in the October 31, 2017 sample was nearly 1000 µM, almost twice the maximum "bloom values" found at either station BP or J01 throughout the 15-month study period. It is also possible that stormed induced increases in freshwater discharge from the Everglades could cause an increased terrigenous DOC flux in northern Florida Bay which could cause total concentrations to increase and extend further south into the Bay resulting in the elevated concentration observed at MB1 (Appendix 4).

While DIN concentrations at all three of our stations are similar throughout the study period, DOC values are elevated significantly at all nine MB stations (453 ± 73 µM average), as compared to BP and Long Key (227 ± 57 µM), based on a 4 station average that included an additional 13th sampling station at the FWC-M dock. The average from the MB area, 453 ± 73 µM, is representative of both stations inside and out of the silled basin, therefore, the residence time of the basin water column does not appear to be a factor in the elevated DOC concentrations. For the concentration to be higher in the central Florida Bay region including all MB stations than at BP and J01 there must be a larger source of DOC or a mechanism for DOC pooling and or preservation. As suggested above, one possibility for a larger source of DOC in central Florida Bay is DOC-enriched water from the Everglades flowing into Florida Bay. Total Organic Carbon (TOC) from the SERC study (Appendix 4) shows a higher concentration of TOC, a summation of DOC and Particulate Organic Carbon, closer to the Everglades than by the Keys island chain further to the south. Although this does not prove the Everglades to be the source of DOC in MB, this possibility should be explored further. Another possible factor that could explain the lower DOC concentrations at BP and J 01 is dilution by oceanside waters from nearby inlets including Tom's Harbor Cut (Fig. 6a). The less reactive fraction of DOC expected to persist in the absence of blooms in the surrounding region could produce the steady concentrations found at these nearshore stations.

Comparison of Post-Irma Results with Florida Bay Baseline Data

The Southeast Environmental Research Center (SERC), a part of the Institute of Water and Environment at Florida International University (FIU) has conducted water quality measurements on monthly to quarterly time scales at multiple sites in Florida Bay for over 25 years (e.g. Boyer 1999; Briceño and Boyer 2010). The SERC data provides baseline information needed to determine trends in Florida Bay nutrient concentrations and other parameters for periods of months to decades. Quarterly data from multiple SERC stations immediately surrounding the three representative stations was collected over a wide range of months and can produce long-term monthly trends when averaged on a canonical basis over the 25-year period, from the late 1980s to July 2017. These SERC results will be used for baseline comparisons with this post-Irma study.

Data from our BP and Long Key sites are similar in concentrations and temporal trends of DIN, Chl-a, and DOC (Fig. 3 and 5) during non-bloom or stormy weather conditions. Averaged data from the SERC BKB stations (green circle map marker, Fig. 6a) were used to create a baseline for these two nearshore stations (yellow thumbtack icons, Fig. 6a). SERC data from the WFB (red square icon, Fig. 6b) and Southern Florida Bay (SFB, yellow diamond icon) stations were used to calculate baseline data for MB1 (yellow thumbtack, Fig. 6b). The SERC data used for baseline data comparisons at all of our sites were chosen to account for both geographic proximity and patterns in biochemical parameters. In the present study we will compare temporal changes in DIN concentrations following Hurricane Irma and other major storm events to the earlier SERC baseline data to understand what impacts major storms and bloom events can have on nitrogen budgets and water quality in Florida Bay. Our results should provide a better understanding of how Florida Bay responds to these episodic events. The monthly averaged data for each SERC station located within the groupings described in Fig. 6 are shown in Fig. 7. Values outside the range of four times the standard deviation (SD) added to the average has been eliminated from the data set (Blaedel et al. 1951).

Averaged DIN and Chl-a at BP, J01, and MB1 are compared to the multi-year, canonically averaged SERC data set in Fig. 8 and 9, respectively. The gray shaded region represents a range from the minimum value of the measured parameter to three times the SD added to the average concentration, while the yellow shaded region represents one SD from average. Following Hurricane Irma, MB had significantly high chl-a and low DIN compared to the multi-year average, while the nearshore sites have high DIN. On Dec 5, 2017 our data agrees with the SERC BKB DIN average concentration, however one week later, after a persistent wind storm, the DIN concentration increases to values nearing three times the SD above the average, an increase of over 300%. I hypothesize that this comparison reveals the impact of NH_4^+-rich porewater injection occurring during sediment suspension that results from persistent wind events.

Starting in January 2018, and throughout the rest of the study, the monthly data agrees with the 25 year SERC patterns found in DIN. Most Chl-a concentrations measured during this study have lower values than the expected from the multi-year study except during bloom events, this could be a result of phytoplankton cell lysing of phytoplankton during freezing of unfiltered samples, although the samples filtered prior to freezing also experienced lower than average concentrations. The SERC pattern includes a spike in DIN concentrations in the early-to-mid Fall as well as increased relative Chl-a in October at MB1. The Chl-a increase in WFB SERC data occurs in association with an increased DIN concentration the prior month. The data presented in this study agrees with these patterns in the SERC data. The early fall increase in DIN is most likely attributable to increased temperatures, most likely due to increased biological activity including microbial processes increasing available DIN. A diminished temporal variability in our 2018 data also agrees with the SERC BKB Chl-a data, that indicates a slight increase in phytoplankton biomass in July as well as in December. Further investigation into the observed winter increases will be needed to determine if this phenomenon is a regular, annual occurrence.

Impacts of Hurricane Irma

A comparison between the long-term SERC data and post-Irma DIN and Chl-a measurements on Oct 31, 2017 for the three stations is shown in Fig. 10. At BP and J01 there was a significant increase in the DIN concentration while the Chl-a remained within error of the SERC BKB long-term average. Our data suggests, Hurricane Irma did not produce an “official” bloom event at our nearshore sites based on the algal bloom threshold of 1.059 µg/L suggested by Boyer et al. (2009) for the majority of south Florida Bay representing the 75th percentile of chlorophyll-a concentrations a multi-year study, which is not significantly different for the concentrations found at BP and J01 on Oct 31, 2017. The algal bloom threshold for the MB field site is 2.845 µg/L (Boyer et al 2009) and our measurement on October 31, 2017 from MB1 post-Irma was 8.58 µg/L, more than three times this value signifying an official bloom. The enhanced primary production led to a significant drawdown of DIN as previously observed at MB stations during 2013-2014 (Hoer 2015). The comparisons shown in Figure 10 suggest that separate regions experience different responses to large storms: increased DIN concentrations occurred at the nearshore sites while interior basin sites experienced more intense phytoplankton blooms that drew down DIN concentrations. A direct comparison of the monthly nutrient concentrations to the SERC data (Fig. 8 and 9) shows DIN results from our field stations closely align with the SERC averages during January and February. This return to baseline SERC values after a few months agrees with a similar recovery period previously witnessed by our group during the 2013-2014 bloom (Hoer 2015).

We initially hypothesized that the nearly complete sponge removal at Burnt Point and other nearshore embayments by Hurricane Irma would eliminate a major source of recycled DIN and that a similar sponge biomass loss at Mystery Basin during 2013 would allow for a direct comparison of changes in nitrogen cycling. Results from the 2013-2014 bloom study in Mystery Basin (Hoer 2015) proved that a large component, 48 ± 24 %, of the total DIN source demand by primary producers had been provided through organic matter recycling by sponges before they were killed off. The sponge losses in Mystery Basin were caused by the phytoplankton bloom that created anoxic bottom waters for an extended time plus slowed sponge pumping due to clogging of tissue from high particulate load (Butler et al. 1995). Four months after the bloom, DIN concentrations stabilized and returned to a new reduced DIN baseline, 43% of the pre-bloom concentrations. Similarly, four months after Hurricane Irma passed over our BP site, removing 95 ± 5 % of the sponge biomass, the concentration of DIN stabilized. However, unlike Mystery Basin in 2013, the average DIN concentration for BP has not decreased with the 95% removal of sponge biomass and remains within the SERC average range for the area. Further investigation of difference in sponge speciation between the two sites could explain this difference in new baseline DIN concentrations between MB and BP stations. At the pre-2013 bloom MB stations, 12% of the sponge biomass was composed of the sponge Geodia gibberosa, (Hoer 2015) this species was not present in BP. G. gibberosa produces 100 ± 20 μmol N hr^{-1} L_{sponge}^{-1} which accounts for the majority of the sponge DIN flux recorded in pre-bloom MB. It appears that the removal of G. gibberosa at MB stations during 2013, caused the lowering of the baseline DIN seen there and not at the BP station in 2017.

Sediments as an Episodic Major Source of DIN

At Florida Bay sites with low sponge biomass or sites with sponges that do not produce a high DIN flux, microbial nutrient regeneration in the sediments appear to have the largest impact on DIN concentrations to the overlying waters. The majority of sediments in Florida Bay are composed of biogenic carbonate muds (Bosence 1989) with an average porosity of 0.81 (Yarbro and Carlson 2008). However, the organic matter content and porosity of Florida Bay sediments varies significantly because of the occurrence of a wide variety of sediment types featuring highly variable grain size, organic matter composition, and deposition rates (Prager and Halley 1997). The average diffusive flux of DIN from bare sediment in Florida Bay was estimated to be 40 μmol N m-2 day -1 by Capone et al. (1992), and the average porewater concentration of NH_4^+ determined by Fourqurean et al. (1992) at multiple sites throughout the Bay was 78.6 μM. The large sediment porewater NH4+ reservoir should be capable of supplying the benthic macroalgae and phytoplankton with a major portion of their DIN requirement. The N demand of seagrasses and macroalgae in central and eastern Florida Bay appears to be largely met due to direct supply from these elevated concentrations in the sediment (Fourqurean et al 1992). However, when a storm stirs the sediment, NH_4^+-rich porewater released back into the water column should greatly increase the concentration of DIN in the shallow water column. I hypothesize that an increase in water column DIN caused by sustained wind events over 15 m/s creates nutrient-rich conditions highly susceptible to bloom activity, especially if other key parameters such as soluble reactive phosphorus (SRP) and bloom-favored species of phytoplankton are available. Prager and Halley (1997) describe Florida Bay sediment distributions using eight bottom types based on grain size and organic matter content, allowing for generalization as to which areas might support significant sediment-water column fluxes of NH4+. We collected whole wet sediment samples from five different sediment types at field sites BP and MB1 (Fig. 11) in September 2018, in order to gain a qualitative sense of potential NH4+ sediment-water fluxes. We found that the variety of heterogeneous sediment types across just two sites could support a significant flux of NH_4^+ as observed concentrations derived from these samples reached 100s of μM after incubating the sediment sample in the laboratory for just a few days. Future work could include similar laboratory incubation experiment to determine NH4+ production rates in the sediment for comparison with sediment-water fluxes calculated from measured concentration gradients in the various sediment types.

The natural diffusive flux of DIN, almost all in the form of NH_4^+, from each sediment type into the water column could be relatively small as compared to other sources. However, even modest storms with sustained winds over 15 m/s would be expected to release significant quantities of NH4+ rich porewaters as a result of resuspension of the upper 3 to 5 cm of the sediment column, creating potentially large spikes in DIN concentrations in the water column. The NOAA buoy at Long Key (LONF1) has recorded 576 days with wind gusts greater than 15 m/s since 2001, averaging a potential resuspension event about every two weeks. The storm we witnessed on December 9, 2017 had gusts over 15 m/s, turned the water column milky white because of sediment resuspension, and probably caused the significant DIN increase we observed (Fig. 3) at our nearshore sites. The frequency of the storm events sparked interest in estimating the potential impact of the wind resuspension and our ability to quantify the release of

DIN from the sediment. We performed “shake” experiments and collected sediment cores at our BP station (Fig. 12) in order to estimate the concentration of NH_4^+ released from sediment resuspension at our sites. The ambient concentrations of NH_4^+ in the water column at BP was 0.82 ± 0.08 μM, during the sediment coring and shake experiment performed on June 25, 2018. The shake experiment produced a 50% increase in NH_4^+ concentrations over the ambient value (1.29 ± 0.06 μM), revealing that a release of NH_4^+ may occur with the resuspension of sediment. The purpose of the coring experiment was to assess the NH_4^+ content of the porewater nitrogen pool, both in terms of its depth distribution in the sediments as well as the total DIN reservoir held in the upper sediment. The core experiment revealed that sediments at 2, 3.5, and 5 cm had concentrations of 12.28 ± 1.12, 33.18 ± 2.39, and 35.35 ± 6.73 μM respectively. These DIN concentrations are uncorrected for mineral adsorption of NH_4^+ and therefore represents a fraction of the total potential DIN available. The concentrations found were are much larger than those typically found in the ambient water column, up to 4000% in this experiment, and we noted that they are minimum values compared to those previously found by Fourqurean et al. (1992) of 78.6 μM. The difference between the NH_4^+ concentrations at 3 cm and 5 cm depth in the sediment were not significantly different, therefore the largest change in the nitrogen pool at station BP occurs between 2 and 3.5 cm of the sediment surface. Fourqurean et al. (1992) previously found no spatial heterogeneity in concentrations versus sediment depth, while we found a large difference within the first few centimeters of sediment, but leveling out before 3.5 cm. Because of the findings in the shake and core experiments, we conclude that sediment resuspension caused by Hurricane Irma was a leading factor in the increased DIN found in our October 31, 2017 samples at BP and J01, relative to non-storm periods found previously (Boyer 1999, Fourqurean 1993).

A large storm event that resuspends sediment might not always result in a bloom because of variable nutrient limitation. At least parts of the Central and Western Florida Basins are nitrogen limited and a significant introduction of NH_4^+ from the sediments during the storm could cause bloom conditions in these regions. Station MB1 which is located in WFB (Fig. 1) experienced a bloom after Hurricane Irma passed over Florida Bay. On the other hand, both the Back Key Basin stations, BP and J01 (Fig. 1), experienced increased levels of DIN after Hurricane Irma and the December wind event, but not an immediate resultant bloom. This may be due to phosphorus limitation or the lack of a significant population of bloom species in the region at the time of the spiked DIN concentrations. Physical mixing between regions of Florida Bay might enhance algal growth potential over large areas because of greater connectivity through surface water transport. Central Florida Bay lies between regions of differing phosphorus versus nitrogen limitation (Briceño and Boyer 2010), with added nutrients from sediments increasing the potential for algal blooms. Mystery Basin is located near the border of western and central Florida Bay which could cause MB1 to experience more frequent and more intense blooms because this area can regularly have nutrient ratios approaching Redfield values due to physical mixing. Phytoplankton blooms are the most common in October to January as a result of wind-driven movement of phytoplankton rich waters out of the Central Florida Bay into the Southern and Western portions of the Bay (Hitchcock et al 2007). Through this transport across the Central Basin, a bloom could result in the Southern basin where BP and J01 are located, and where increased DIN from storms could allow the bloom to persist. Bloom conditions are known to shift in response to dominant prevailing wind directions (Phlips et al 1999). Such transport could cause blooms to spread into other regions of Florida Bay, including the southern Bay which is not nitrogen limited, to experience bloom conditions after a large resuspension event elsewhere in the Bay.

Conclusions

The primary objective of the present study was to understand how Hurricane Irma impacted concentrations of DIN, DOC, and Chl-a in the Florida Bay ecosystem, including the potential impacts of phytoplankton blooms and sponge biomass loss. In order to achieve this objective, I sought to compare results from a 15-month study that followed Hurricane Irma with 25 years of quarterly monitoring data collected through the SERC program during 1989 to 2017. Monthly collections of water column samples at fixed sites, chosen to represent nearshore and central basin environments, revealed that changes from long-term baseline concentration caused by persistent storms, including Hurricane Irma, have immediate impacts that dissipate within months. As a result of Hurricane Irma, interior locations of Florida Bay experienced large-scale phytoplankton blooms and low DIN concentrations, while in contrast, increased DIN concentrations occurred at nearshore stations without creating quick resultant blooms. Hurricanes and other persistent storms can cause immediate spikes in water column DIN concentrations though sediment resuspension which releases large quantities of NH_4^+ stored in the porewaters in the upper 5 cm of the underlying sediment column.

Dramatic sponge biomass losses occurred at bloom and Hurricane Irma impacted stations in Florida Bay. The extent of the impacts of the biomass losses on DIN recycling to the overlying water column depends upon sponge speciation and which nutrient element is limiting to primary production in a given area of the Bay.

High concentrations of both DIN and Chl-a generally occur during summer months in Florida Bay, while winter values are typically lower. The reservoir size, natural flux, and storm induced fluxes of NH_4^+ out of sediment may change with sediment types, therefore, more research is needed to assess the importance of this source. The sources and importance of nutrients to shallow Florida Bay change as a result of blooms, natural disasters, and inland runoff from the Everglades. Changes in the temporal variability and strengths of these episodic events may produce greater and more lasting impacts. The data in this study came from sites that represent only a small percentage of the total area of Florida Bay. Many additional factors, including more complex physical, biochemical, and geological processes not fully discussed in this project are likely to affect concentrations of DIN, DOC, and Chl-a. Longer time-series studies, including the collection of larger-scale, time-series data sets will lead to a better understanding of the responses of Florida Bay to episodic events.

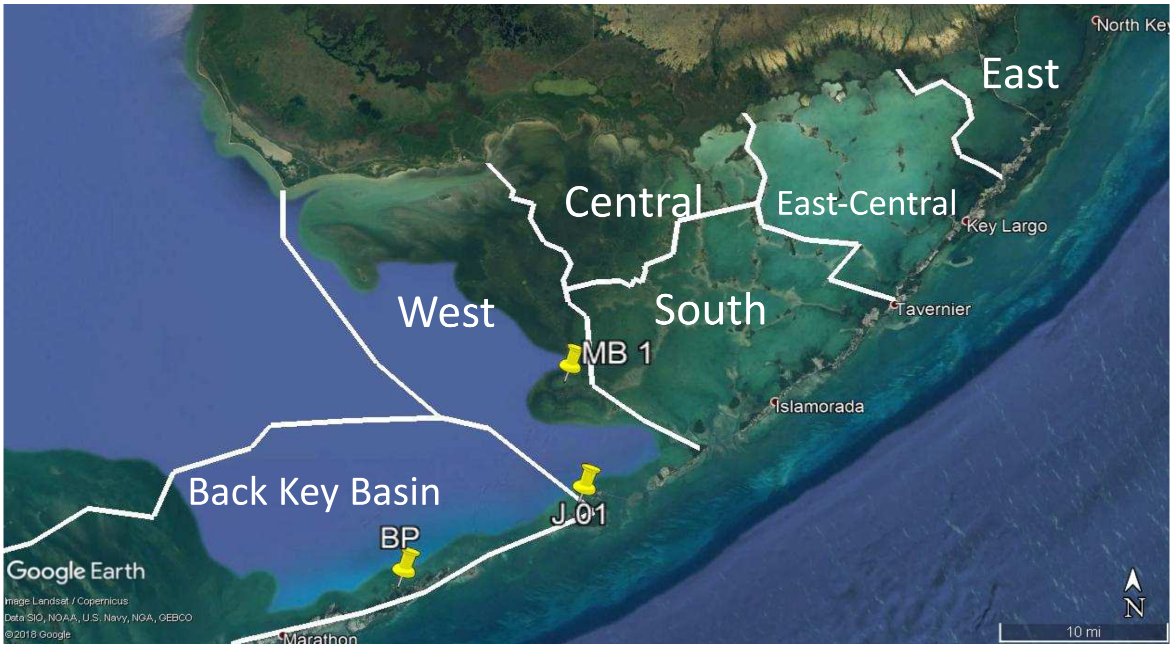


Figure 1: Regions of Florida Bay. Outlined regions of Florida Bay according to Briceño and Boyer (2010, 2013). The field sites in this study are located in the Back Key Basin and West regions.

Figure 2: Field Site Maps. These maps show the locations of monthly field collection stations at our three different sites, a.) Mystery Basin b.) Burnt Point Embayment c.) Long Key Nearshore. GPS coordinates in Appendix 2.

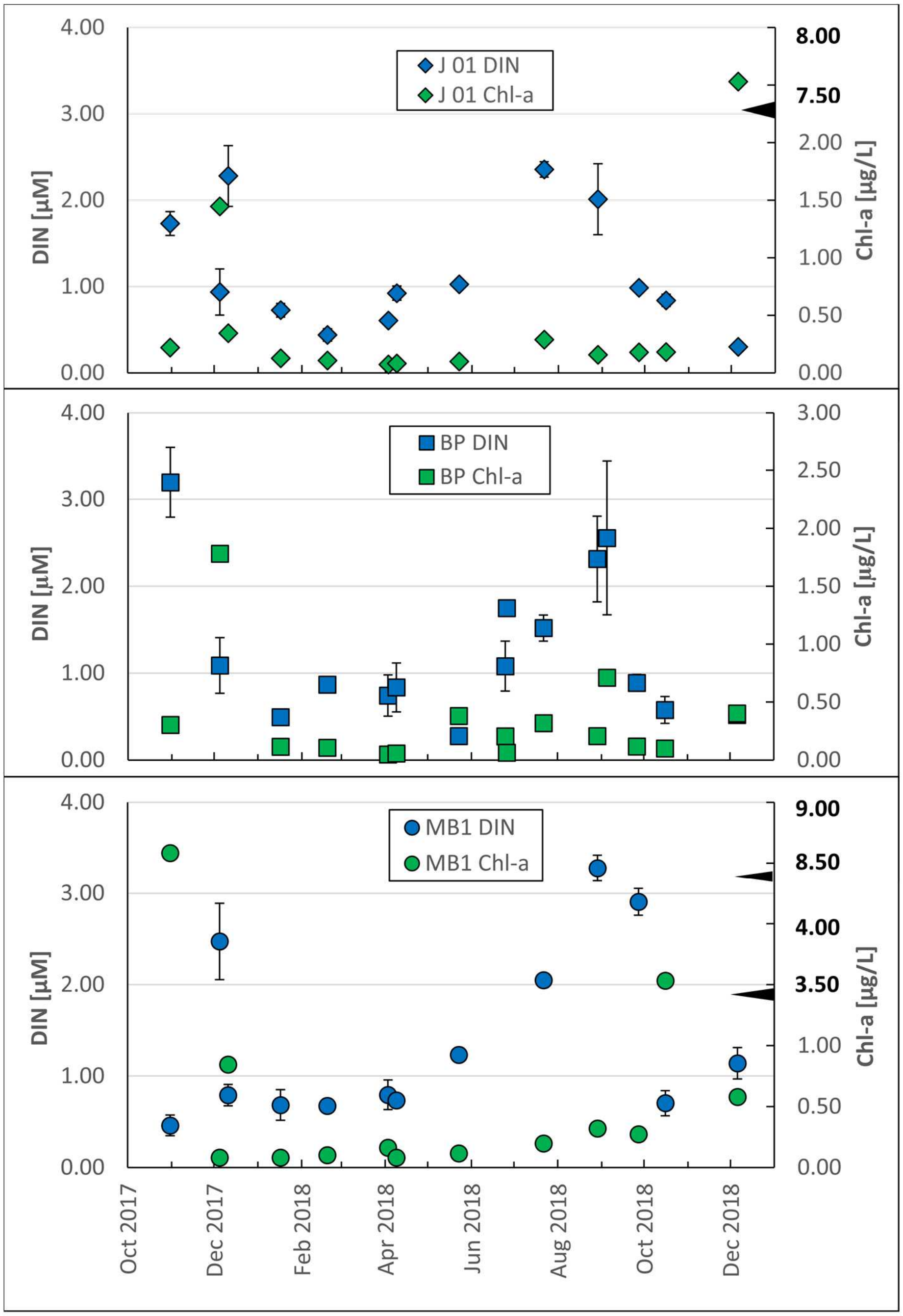


Figure 3: Monthly Collection DIN Concentrations. The primary axis displays DIN concentration [µM] at stations J01, BP, and MB1, while the secondary plots Chl-a [µg/L]. Error bars represent 1 SD from the average. Panel (a) and (c) has a break in the Chl-a axis to capture bloom events.

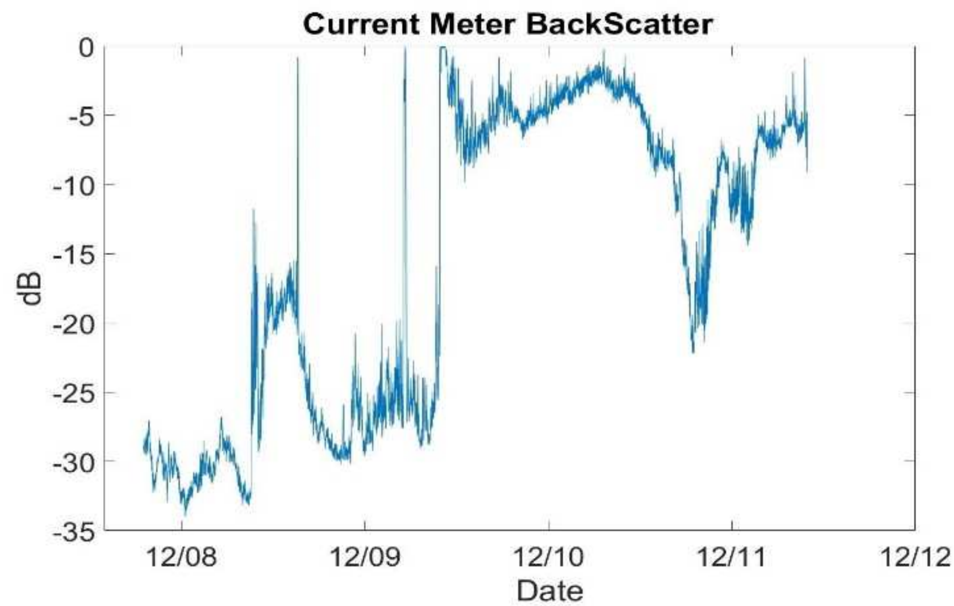


Figure 4: ADCP Backscatter Signal. Measurements of the backscatter signal from an ADCP Sensor located in Burnt Point (December 2017). The backscatter data is used as a proxy for sediment resuspension as it represents particle load in the water column. The resuspension event is marked by the harsh increase the night of December 9, 2017.

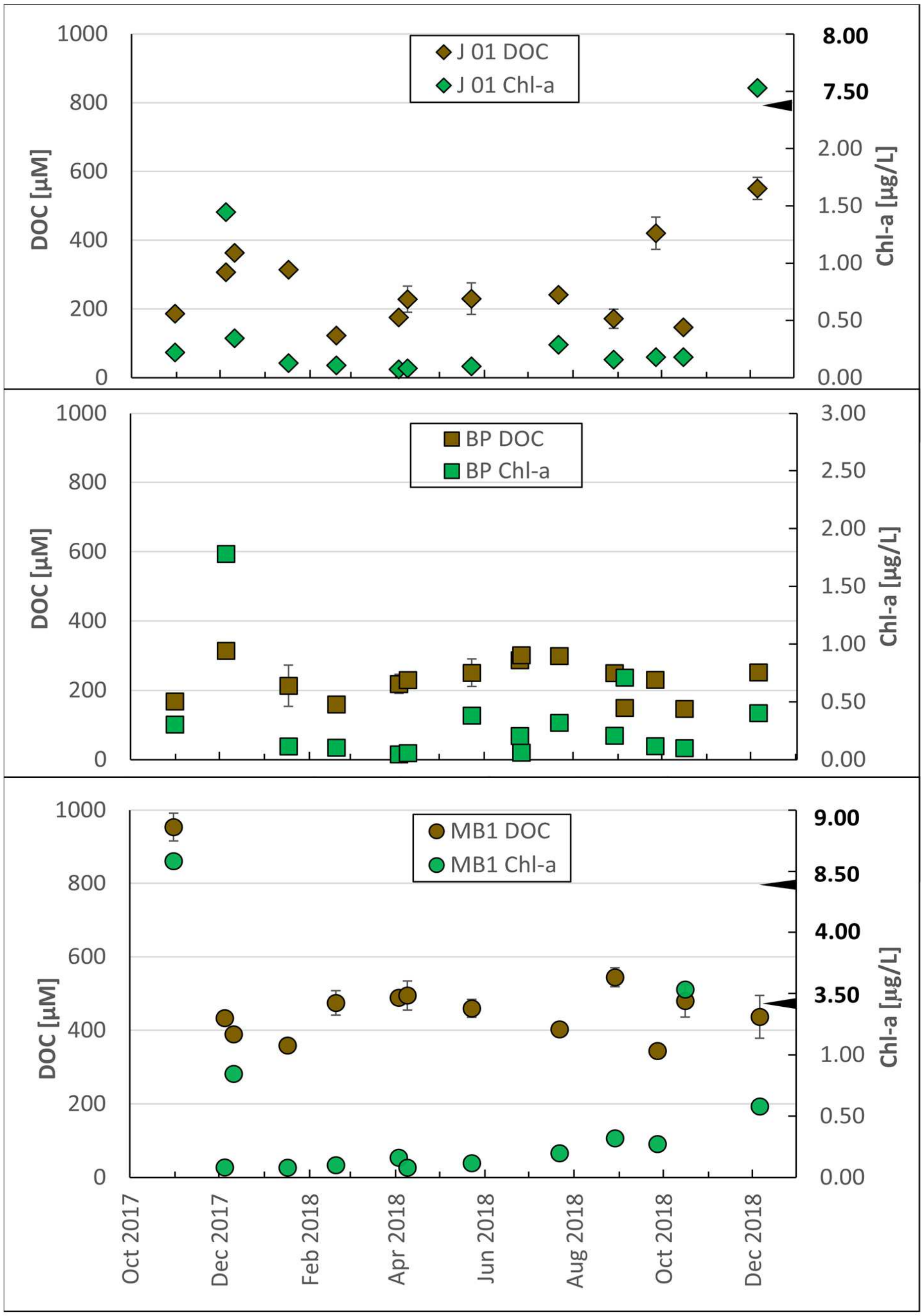


Figure 5: Monthly Collection DOC Concentrations. The primary axis displays DOC concentration [µM] at stations J01, BP, and MB1, while the secondary axis shows Chl-a concentrations [µg/L] in order to qualify the data presented. Error bars represent 1 SD from the average. Panel (a) has a break in the Chl-a axis to capture a bloom at J01 in Dec 2018. The scales on plot (c) for MB1 are larger for both DOC and Chl-a than those in plots (a) and (b).

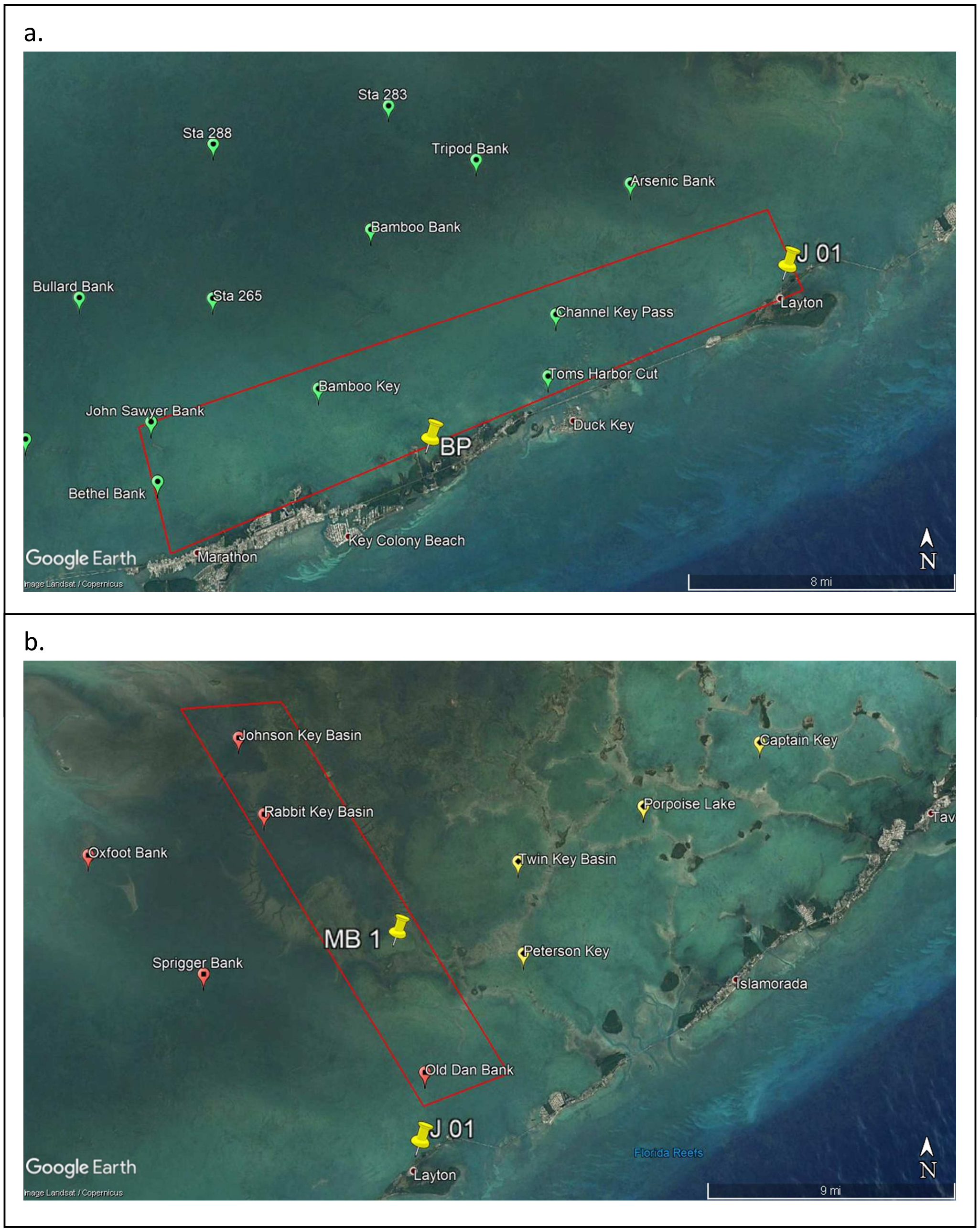


Figure 6: SERC Field Sites and Stations. The map displays SERC stations (BKB: Green Circles, WFB: Red Squares, SFB: Yellow Diamonds) (Briceño and Boyer 2010, 2013) in relation to our field sites. The red regions represent the areas used for SERC data baselines for (a) BP and J01 or (b) MB1 based on geographic proximity and biochemical patterns (Fig. 7).

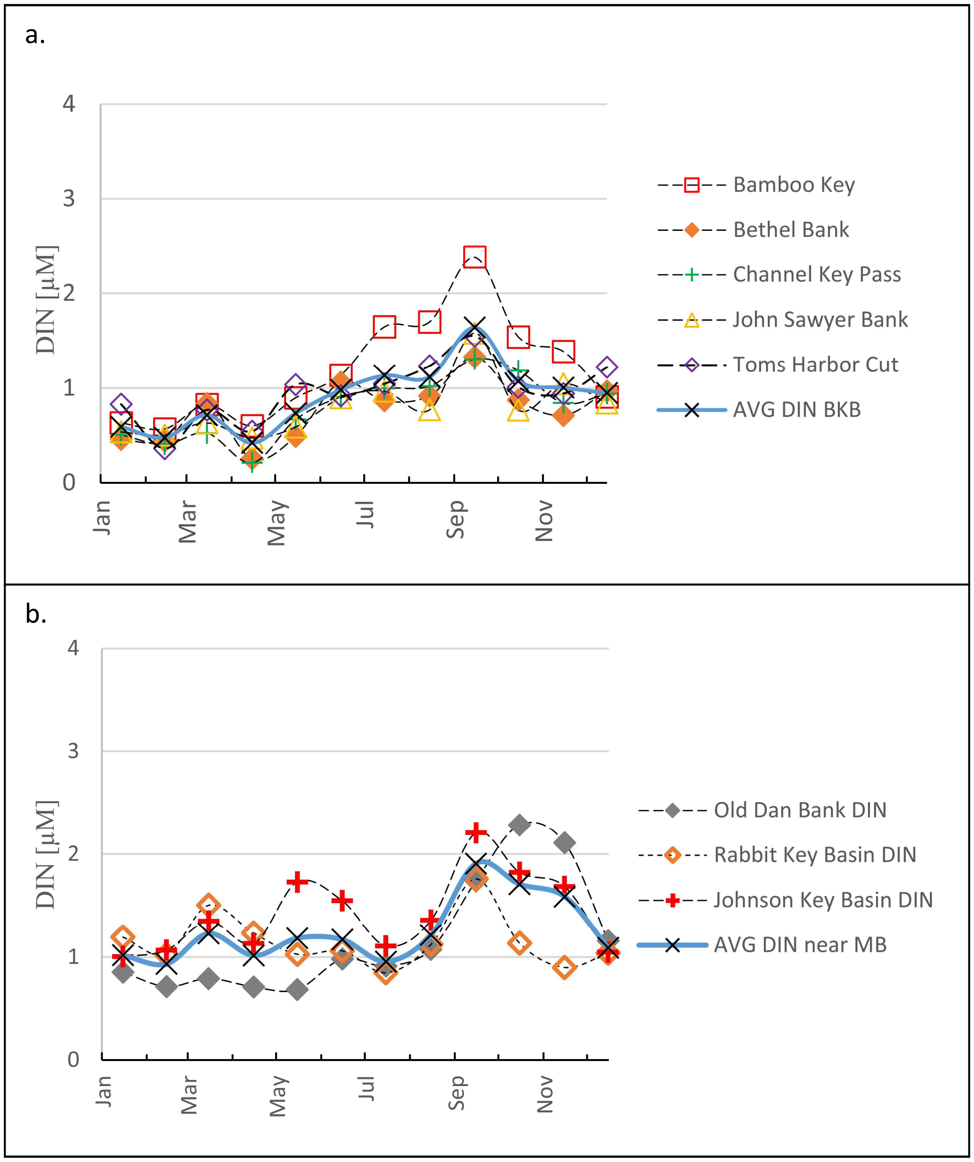


Figure 7: SERC Station Monthly Averages. DIN concentrations [µM] plotted on monthly averages for each of the SERC stations located within the baseline areas (outlined in red in Fig. 6). The stations are collectively averaged to give the baseline for each area (Fig. 6) denoted by the AVG DIN solid line in both graphs, (a) Burnt Point/J01 and (b) Mystery Basin

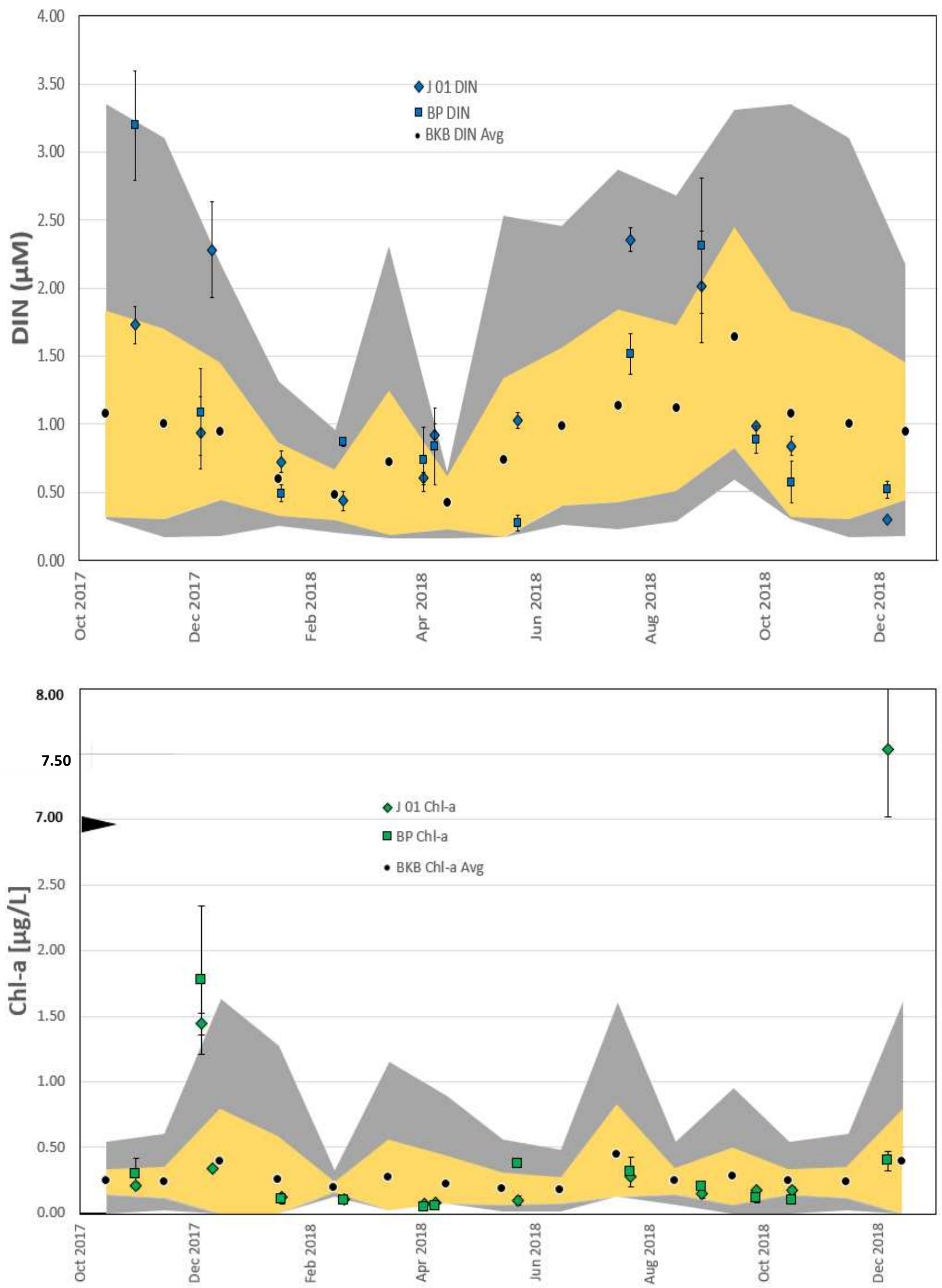
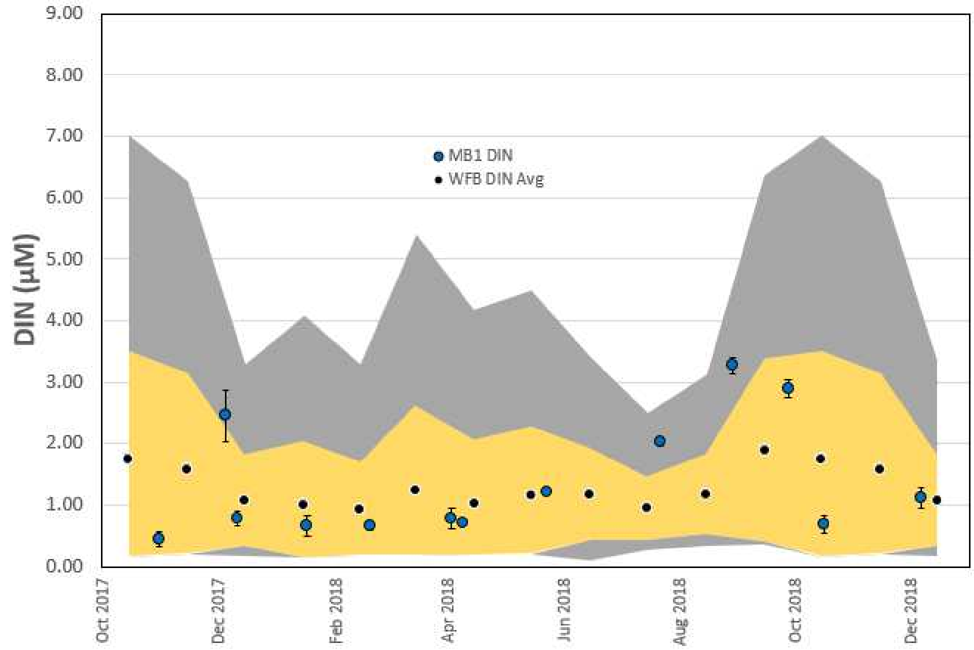


Figure 8: BP and J01 DIN and Chl-a Concentration Comparison with SERC Averages. The SERC monthly averages were extended to fit the 15-month study. The yellow shaded regions represent the 1SD from the average SERC BKB data. The grey shaded regions represent the SERC BKB minimum measured concentration to three times the standard deviation added to the average concentration. Error bars represent 1 SD from the average. Panel (b) has a break in the axis to capture a bloom at J01 in Dec 2018.



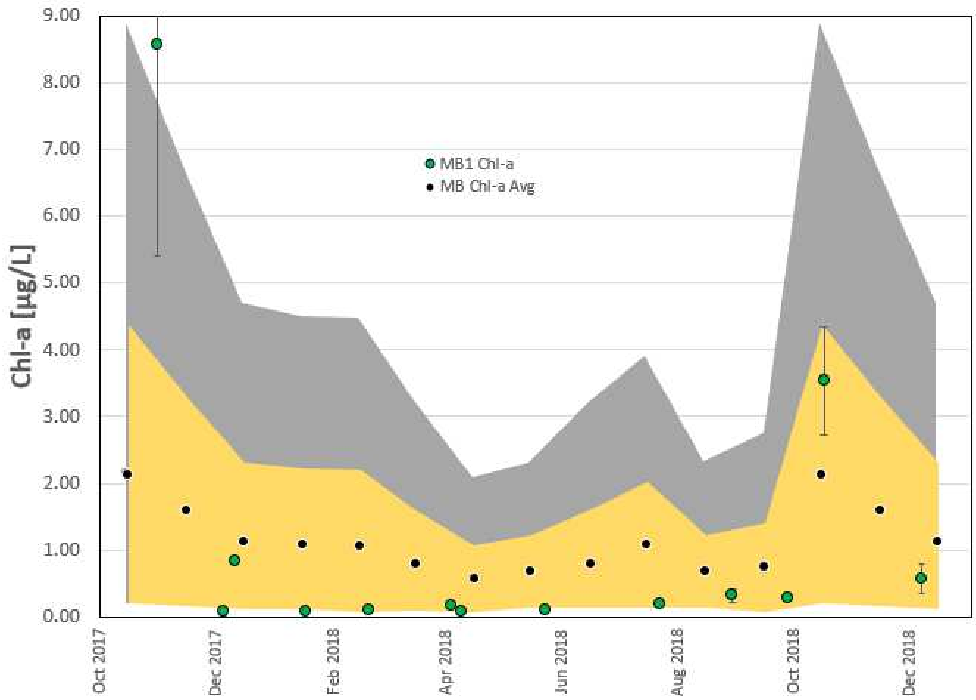


Figure 9: MB1 DIN and Chl-a Concentration Comparison with SERC Averages. The SERC monthly averages were extended to fit the 15-month study. The yellow shaded regions represent the 1SD from the average SERC BKB data The shaded regions represent the SERC BKB minimum measured concentration to three times the standard deviation added to the average concentration. Error bars represent 1 SD from the average.

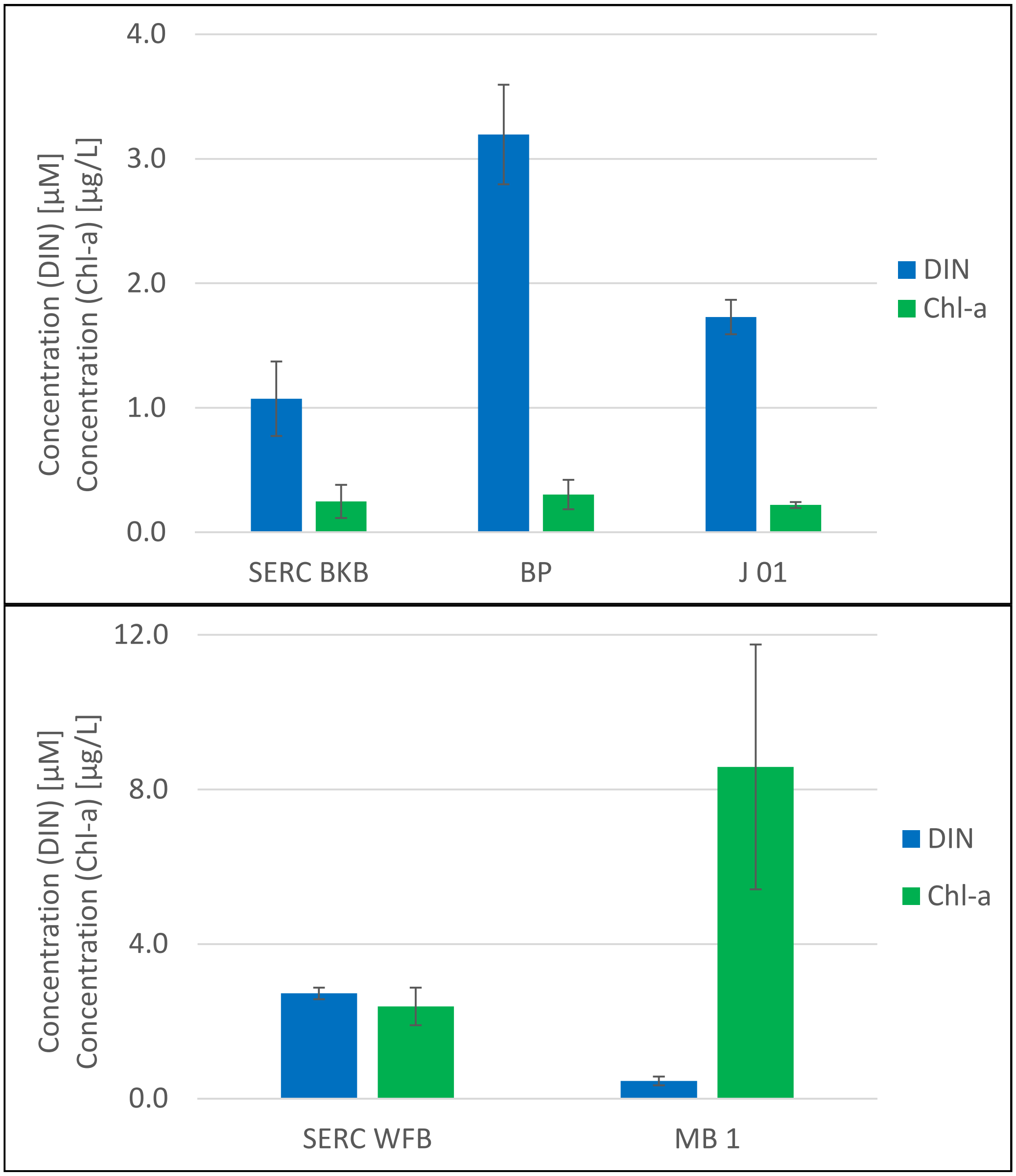


Figure 10: Hurricane Irma Comparison with SERC Averages. The top panel compares SERC BKB sites to BP and J01. The DIN concentrations in both study sites is significantly larger than the SERC BKB average, while the chl-a is within the long-term average. The bottom panel displays the SERC WFB comparison to MB1, where chl-a concentration is more than twice the average SERC WFB and the DIN concentration is significantly depleted as a result of the bloom. Error bars represent 1 SD from the average.

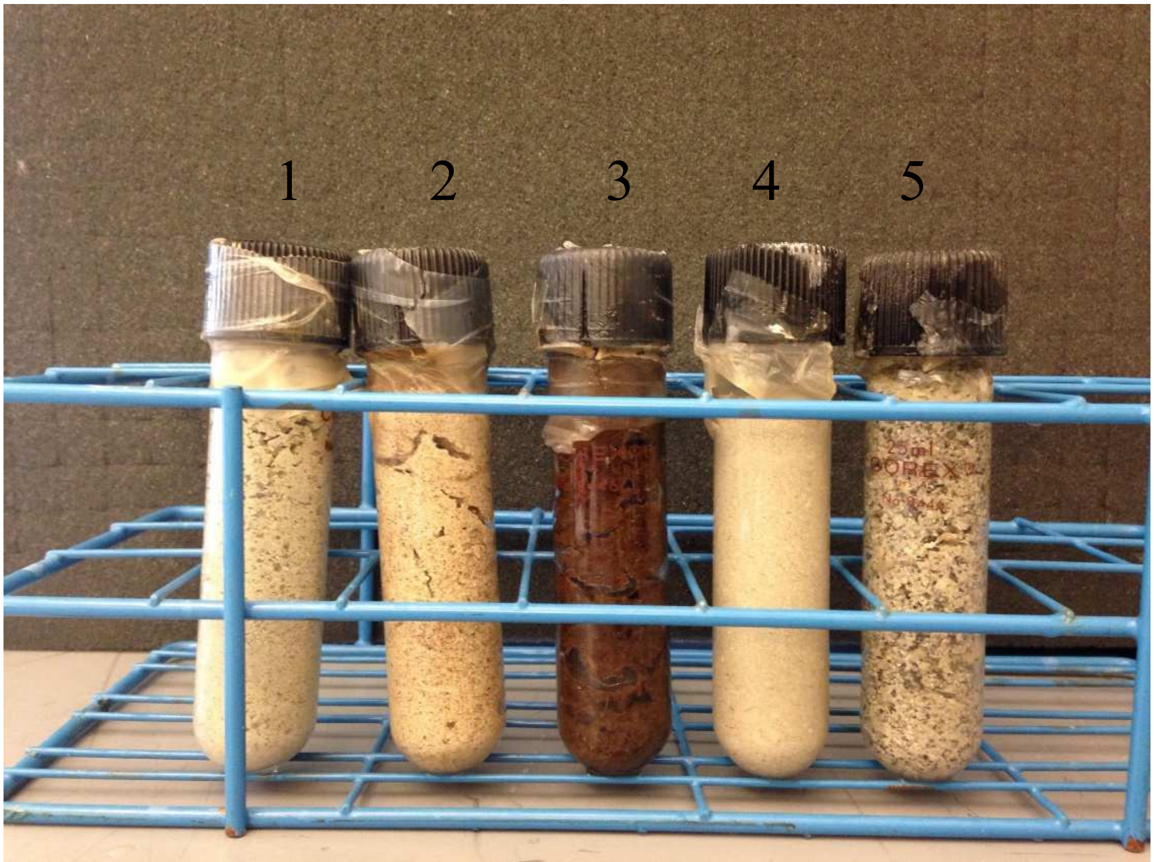


Figure 11: Sediment Types Across Florida Bay. Five sediments types that were collected from sites BP (1,2,3) and MB (4,5). 1.) Hardbottom 2.) Course Mud 3.) Mangrove 4.) Dense Seagrass 5.) Sparse Seagrass

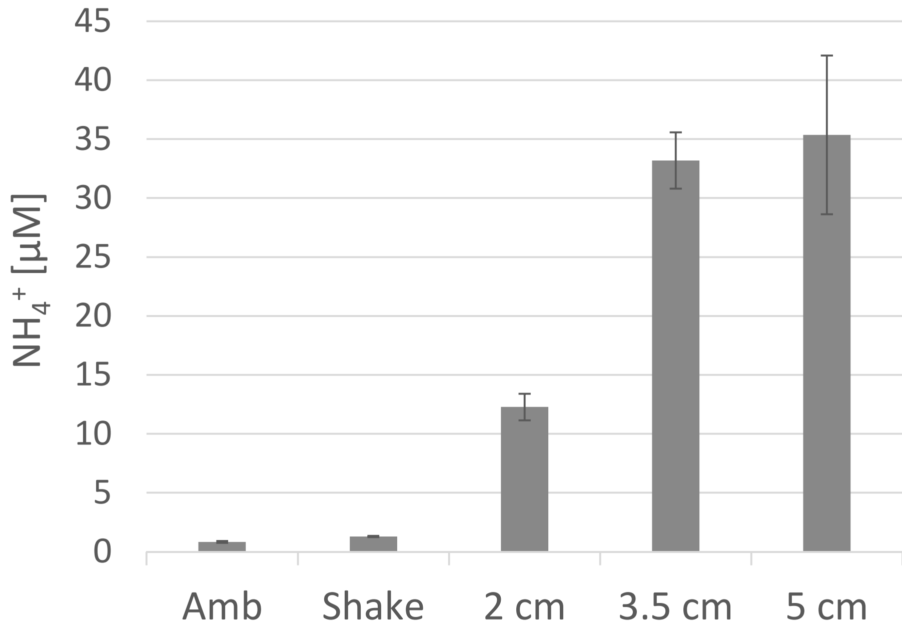


Fig. 12 Shake and Core Experiments. Conducted on June 25, 2018 at station BP. Amb represents the ambient overlying water in BP, shake represents the experiment described in the method section where a 5-sdied acrylic cube was scraped back and forth over the sediment to simulate storm advection, and the core sizes represent the three sediment core sizes used to measure the concentration of ammonium in the sediment. Error bars represent 1 SD from the average.

APPENDIX 1: TABLE OF MONTHLY COLLECTION DATA

Date	Station	NOx^- (µM)	NH_4^+ (µM)	DIN (µM)	DOC (µM)	TN (µM)	Chl-a (µg/L)
Oct 31, 2017	MB1	0.44 ± 0.11	0.03 ± 0.025	0.46 ± 0.11	954 ± 38	68 ± 4	8.58 ± 3.17
Dec 5, 2017	MB1	0.72 ± 0.25	1.75 ± 0.34	2.47 ± 0.42	433 ± 11	30 ± 1	0.08 ± 0.07
Dec 11, 2017	MB1	0.52 ± 0.11	0.27 ± 0.02	0.79 ± 0.12	389 ± 5	25 ± 1	0.85 ± 0.02
Jan 17, 2018	MB1	0.47 ± 0.15	0.21 ± 0.08	0.68 ± 0.17	359 ± 6	26 ± 3	0.08 ± 0.01
Feb 19, 2018	MB1	0.39 ± 0.07	0.29 ± 0.01	0.68 ± 0.07	475 ± 33	29 ± 3	0.10 ± 0.04
April 3, 2018	MB1	0.18 ± 0.06	0.61 ± 0.15	0.79 ± 0.16	489 ± 18	62 ± 11	0.16 ± 0.01
April 9, 2018	MB1	0.23 ± 0.03	0.50 ± 0.04	0.73 ± 0.04	495 ± 40	41 ± 6	0.08 ± 0.03
May 23, 2018	MB1	0.26 ± 0.03	0.97 ± 0.03	1.23 ± 0.03	460 ± 24	36 ± 11	0.12 ± 0.01
Jul 22, 2018	MB1	0.29 ± 0.06	1.76 ± 0.08	2.05 ± 0.08	403 ± 14	37 ± 1	0.20 ± 0.04
Aug 29, 2018	MB1	1.20 ± 0.57	2.08 ± 0.14	3.28 ± 0.14	544 ± 26	42 ± 2	0.32 ± 0.10
Sept 27, 2018	MB1	0.73 ± 0.07	2.18 ± 0.15	2.91 ± 0.15	344 ± 6	40 ± 5	0.27 ± 0.01
Oct 16, 2018	MB1	0.32 ± 0.04	0.39 ± 0.14	0.70 ± 0.14	480 ± 44	41 ± 3	3.53 ± 0.81
Dec 6, 2018	MB1	0.45 ± 0.06	0.69 ± 0.17	1.14 ± 0.17	437 ± 58	10 ± 2	0.58 ± 0.22
Oct 31, 2017	MB2	0.64 ± 0.09	0.07 ± 0.02	0.71 ± 0.09	884 ± 39	60 ± 3	6.63 ± 2.94
Dec 5, 2017	MB2	1.33 ± 0.34	2.90 ± 0.66	4.23 ± 0.74	467 ± 24	39 ± 4	0.25 ± 0.08
Dec 11, 2017	MB2	1.34 ± 0.28	0.43 ± 0.01	1.77 ± 0.28	387 ± 7	31 ± 12	0.76 ± 0.23
Jan 17, 2018	MB2	0.32 ± 0.08	0.23 ± 0.01	0.55 ± 0.08	327 ± 9	22 ± 2	0.06 ± 0.01
Feb 19, 2018	MB2	0.23 ± 0.09	0.53 ± 0.02	0.76 ± 0.09	470 ± 75	31 ± 6	0.18
April 3, 2018	MB2	0.45 ± 0.13	0.31 ± 0.03	0.76 ± 0.13	467 ± 19	38 ± 3	0.18 ± 0.01
April 9, 2018	MB2	0.16 ± 0.03	0.10 ± 0.03	0.27 ± 0.04	513 ± 24	61 ± 20	0.20 ± 0.09
May 23, 2018	MB2	0.24 ± 0.04	0.85 ± 0.04	1.09 ± 0.06	393 ± 17	28 ± 4	0.27
Jul 22, 2018	MB2	0.17 ± 0.04	0.95 ± 0.39	1.12 ± 0.39	483 ± 5	44 ± 1	0.34 ± 0.02
Aug 29, 2018	MB2	0.03 ± 0.03	1.28 ± 0.11	1.30 ± 0.11	571 ± 76	44 ± 13	0.34 ± 0.07
Sept 27, 2018	MB2	0.27 ± 0.03	2.00 ± 0.29	2.27 ± 0.29	470 ± 55	40 ± 7	0.36 ± 0.04
Oct 16, 2018	MB2	0.21 ± 0.02	0.12 ± 0.03	0.33 ± 0.02	313 ± 17	28 ± 1	1.32 ± 0.68
Dec 6, 2018	MB2	0.33 ± 0.03	0.71 ± 0.24	1.04 ± 0.24	447 ± 14	9.7 ± 0.6	0.79 ± 0.02
Oct 31, 2017	MB5	ND	ND	ND	ND	ND	ND
Dec 5, 2017	MB5	0.24 ± 0.10	0.65 ± 0.03	0.89 ± 0.11	407 ± 12	29 ± 2	2.35
Dec 11, 2017	MB5	0.63 ± 0.30	0.18 ± 0.01	0.81 ± 0.30	399 ± 14	26 ± 1	1.53 ± .20
Jan 17, 2018	MB5	0.25 ± 0.10	0.16 ± 0.01	0.41 ± 0.10	355 ± 6	23 ± 1	0.05 ± 0.01
Feb 19, 2018	MB5	0.35 ± 0.05	0.29 ± 0.13	0.64 ± 0.14	468 ± 33	28 ± 2	0.14 ± 0.02
April 3, 2018	MB5	0.25 ± 0.03	0.92 ± 0.13	1.18 ± 0.13	464 ± 29	44 ± 10	0.12 ± 0.01
April 9, 2018	MB5	0.19 ± 0.01	0.28 ± 0.01	0.47 ± 0.02	476 ± 29	36 ± 2	0.32 ± 0.30
May 23, 2018	MB5	0.21 ± 0.01	0.71 ± 0.03	0.92 ± 0.03	296 ± 29	21 ± 4	0.10 ± 0.08
Jul 22, 2018	MB5	0.18 ± 0.04	1.43 ± 0.20	1.60 ± 0.20	341 ± 12	33 ± 2	0.36 ± 0.16
Aug 29, 2018	MB5	1.10 ± 0.03	2.08 ± 0.61	3.18 ± 0.61	485 ± 11	42 ± 3	0.40 ± 0.10
Sept 27, 2018	MB5	0.54 ± 0.04	1.31 ± 0.16	1.86 ± 0.17	453 ± 3	44 ± 5	0.32 ± 0.02
Oct 16, 2018	MB5	0.12 ± 0.03	0.03 ± 0.03	0.15 ± 0.03	428 ± 8	35 ± 1	5.15
Dec 6, 2018	MB5	0.27 ± 0.03	0.58 ± 0.04	0.84 ± 0.05	417 ± 13	9 ± 1	0.63 ± 0.06

Date	Station	NOx^- (µM)	NH_4^+ (µM)	DIN (µM)	DOC (µM)	TN (µM)	Chl-a (µg/L)
Oct 31, 2017	MB8	ND	ND	ND	ND	ND	ND
Dec 5, 2017	MB8	0.54 ± 0.20	1.51 ± 0.14	2.05 ± 0.24	429 ± 12	32 ± 7	0.41 ± 0.22
Dec 11, 2017	MB8	0.93 ± 0.15	0.48 ± 0.01	1.41 ± 0.15	435 ± 16	33 ± 4	1.85
Jan 17, 2018	MB8	0.26 ± 0.05	0.21 ± 0.05	0.46 ± 0.07	384 ± 8	26 ± 1	0.08 ± 0.03
Feb 19, 2018	MB8	0.73 ± 0.32	0.78 ± 0.09	1.50 ± 0.34	433 ± 37	27 ± 2	0.30
April 3, 2018	MB8	0.36 ± 0.19	0.75 ± 0.25	1.10 ± 0.31	374 ± 17	37 ± 10	0.16 ± 0.01
April 9, 2018	MB8	0.21 ± 0.09	0.57 ± 0.04	0.78 ± 0.10	433 ± 8	29 ± 1	0.15
May 23, 2018	MB8	0.24 ± 0.03	1.11 ± 0.12	1.35 ± 0.12	452 ± 40	30 ± 7	0.20 ± 0.03
Jul 22, 2018	MB8	0.12 ± 0.03	0.76 ± 0.12	0.89 ± 0.12	361 ± 10	34 ± 2	0.30 ± 0.01
Aug 29, 2018	MB8	0.71 ± 0.03	2.78 ± 1.14	3.49 ± 1.14	538 ± 22	41 ± 8	0.36 ± 0.09
Sept 27, 2018	MB8	0.10 ± 0.02	0.01 ± 0.02	0.12 ± 0.02	537 ± 56	44 ± 1	2.84 ± 0.38
Oct 16, 2018	MB8	0.33 ± 0.04	0.12	0.46 ± 0.04	423 ± 25	37 ± 1	4.49 ± 1.18
Dec 6, 2018	MB8	0.27 ± 0.02	0.57 ± 0.01	0.84 ± 0.01	431 ± 6	9 ± 1	1.26 ± 0.12
Oct 31, 2017	MB9	ND	ND	ND	ND	ND	ND
Dec 5, 2017	MB9	0.03 ± 0.03	1.03 ± 0.07	1.06 ± 0.08	418 ± 7	28 ± 1	0.19 ± 0.07
Dec 11, 2017	MB9	0.47 ± 0.26	0.44 ± 0.01	0.91 ± 0.26	423 ± 5	28 ± 1	1.62 ± 0.57
Jan 17, 2018	MB9	0.31 ± 0.10	0.27 ± 0.01	0.59 ± 0.10	392 ± 25	26 ± 4	0.08 ± 0.01
Feb 19, 2018	MB9	0.27 ± 0.03	0.48 ± 0.01	0.75 ± 0.03	430 ± 130	30 ± 10	0.35 ± 0.01
April 3, 2018	MB9	0.25 ± 0.07	0.82 ± 0.01	1.07 ± 0.07	418 ± 4	45 ± 9	0.15 ± 0.01
April 9, 2018	MB9	0.22	0.30 ± 0.02	0.53 ± 0.02	474 ± 25	39 ± 14	0.17 ± 0.01
May 23, 2018	MB9	0.30 ± 0.07	0.69 ± 0.11	0.99 ± 0.13	459 ± 9	36 ± 2	0.14 ± 0.03
Jul 22, 2018	MB9	0.16 ± 0.08	0.73 ± 0.08	0.88 ± 0.12	333 ± 21	29 ± 3	0.55
Aug 29, 2018	MB9	0.03	2.39 ± 1.82	2.42 ± 1.82	507 ± 70	50 ± 18	0.34 ± 0.09
Sept 27, 2018	MB9	0.13 ± 0.05	0.03 ± 0.03	0.17 ± 0.06	600 ± 10	58 ± 4	3.72 ± 0.11
Oct 16, 2018	MB9	0.20 ± 0.15	0.15	0.35	522 ± 21	42 ± 4	6.40 ± 0.37
Dec 6, 2018	MB9	0.35 ± 0.04	0.89 ± 0.07	1.24 ± 0.08	418 ± 8	9 ± 1	0.87 ± 0.17
Oct 31, 2017	MB10	ND	ND	ND	ND	ND	ND
Dec 5, 2017	MB10	0.54 ± 0.24	0.59 ± 0.06	1.12 ± 0.24	393 ± 3	28 ± 2	0.36 ± 0.09
Dec 11, 2017	MB10	0.44 ± 0.26	0.19 ± 0.01	0.63 ± 0.26	384 ± 4	24 ± 1	2.36 ± 0.65
Jan 17, 2018	MB10	0.56 ± 0.20	0.19 ± 0.01	0.74 ± 0.20	339 ± 3	22 ± 1	0.09 ± 0.00
Feb 19, 2018	MB10	0.31 ± 0.03	0.32 ± 0.01	0.63 ± 0.04	507 ± 21	34 ± 3	0.12 ± 0.01
April 3, 2018	MB10	0.31 ± 0.18	0.55 ± 0.04	0.86 ± 0.19	427 ± 19	39 ± 15	0.11 ± 0.01
April 9, 2018	MB10	0.13 ± 0.07	0.03	0.13 ± 0.07	413 ± 25	27 ± 5	0.15 ± 0.01
May 23, 2018	MB10	0.19	0.66 ± 0.02	0.85 ± 0.02	470 ± 10	36 ± 4	0.17 ± 0.02
Jul 22, 2018	MB10	0.15 ± 0.03	0.93 ± 0.13	1.08 ± 0.13	332 ± 6	30 ± 1	0.36 ± 0.07
Aug 29, 2018	MB10	0.70 ± 0.20	1.46 ± 0.19	2.17 ± 0.19	512 ± 35	39 ± 1	0.24 ± 0.02
Sept 27, 2018	MB10	0.25 ± 0.14	0.21 ± 0.00	0.45 ± 0.00	535 ± 38	43 ± 4	0.55 ± 0.08
Oct 16, 2018	MB10	0.19 ± 0.24	0.03 ± 0.00	0.22 ± 0.00	746 ± 10	61 ± 1	14.93 ± 1.53
Dec 6, 2018	MB10	0.21 ± 0.14	0.51 ± 0.07	0.72 ± 0.07	431 ± 7	9 ± 0	0.34 ± 0.03

Date	Station	NOx^- (µM)	NH_4^+ (µM)	DIN (µM)	DOC (µM)	TN (µM)	Chl-a (µg/L)
Oct 31, 2017	MB12	ND	ND	ND	ND	ND	ND
Dec 5, 2017	MB12	0.24 ± 0.10	0.80 ± 0.09	1.05 ± 0.13	410 ± 8	29 ± 1	0.31 ± 0.12
Dec 11, 2017	MB12	0.46 ± 0.32	0.24 ± 0.03	0.70 ± 0.32	397 ± 12	28 ± 1	0.18 ± 0.07
Jan 17, 2018	MB12	0.21 ± 0.08	0.20 ± 0.07	0.42 ± 0.11	367 ± 13	27 ± 5	0.09 ± 0.02
Feb 19, 2018	MB12	0.33 ± 0.04	0.47 ± 0.13	0.80 ± 0.14	531 ± 12	35 ± 4	0.22 ± 0.01
April 3, 2018	MB12	0.23 ± 0.03	0.61 ± 0.16	0.83 ± 0.17	412 ± 3	35 ± 3	0.13 ± 0.01
April 9, 2018	MB12	0.29 ± 0.21	0.33 ± 0.03	0.62 ± 0.21	539 ± 14	50 ± 9	0.07 ± 0.03
May 23, 2018	MB12	0.28 ± 0.05	0.52 ± 0.21	0.80 ± 0.22	439 ± 53	36 ± 4	0.38 ± 0.33
Jul 22, 2018	MB12	0.19 ± 0.12	1.35 ± 0.12	1.54 ± 0.17	307 ± 10	30 ± 6	0.42
Aug 29, 2018	MB12	0.73 ± 0.08	2.29 ± 0.04	3.02 ± 0.09	564 ± 51	52 ± 9	0.32 ± 0.00
Sept 27, 2018	MB12	0.28 ± 0.16	0.79 ± 0.02	1.07 ± 0.16	465 ± 69	48 ± 1	0.36 ± 0.14
Oct 16, 2018	MB12	0.45 ± 0.22	0.35 ± 0.04	0.79 ± 0.23	313 ± 4	26 ± 1	1.11 ± 0.13
Dec 6, 2018	MB12	1.37 ± 0.06	0.67 ± 0.09	2.04 ± 0.11	394 ± 3	9 ± 1	0.12 ± 0.37
Oct 31, 2017	MB13	0.44 ± 0.15	0.13 ± 0.10	0.57 ± 0.17	716 ± 16	53 ± 3	7.72 ± 0.60
Dec 5, 2017	MB13	0.87 ± 0.25	1.04 ± 0.09	1.91 ± 0.27	491 ± 19	36 ± 1	2.13 ± 0.41
Dec 11, 2017	MB13	0.27 ± 0.13	0.44 ± 0.01	0.70 ± 0.13	413 ± 11	27 ± 1	1.57 ± 0.01
Jan 17, 2018	MB13	0.32 ± 0.04	0.42 ± 0.04	0.74 ± 0.06	363 ± 21	27 ± 6	0.10 ± 0.03
Feb 19, 2018	MB13	0.34 ± 0.03	0.93 ± 0.02	1.27 ± 0.04	487 ± 20	33 ± 3	0.23 ± 0.04
April 3, 2018	MB13	0.20 ± 0.04	0.57 ± 0.11	0.78 ± 0.12	470 ± 5	38 ± 1	0.54 ± 0.07
April 9, 2018	MB13	0.50 ± 0.19	0.51 ± 0.06	1.01 ± 0.20	465 ± 22	29 ± 1	0.19 ± 0.07
May 23, 2018	MB13	0.24 ± 0.10	1.28 ± 0.11	1.52 ± 0.15	475 ± 11	36 ± 2	0.10 ± 0.06
Jul 22, 2018	MB13	0.26 ± 0.02	1.77 ± 0.15	2.03 ± 0.15	439 ± 5	38 ± 1	0.26 ± 0.01
Aug 29, 2018	MB13	0.03	1.74 ± 0.07	1.76 ± 0.07	546 ± 18	48 ± 13	0.33 ± 0.04
Sept 27, 2018	MB13	0.27 ± 0.05	0.55 ± 0.02	0.82 ± 0.06	576 ± 93	58 ± 7	1.32 ± 0.09
Oct 16, 2018	MB13	0.42 ± 0.10	0.74 ± 0.02	1.16 ± 0.10	176 ± 9	16 ± 1	0.08 ± 0.08
Dec 6, 2018	MB13	1.20 ± 0.10	0.62 ± 0.03	1.82 ± 0.11	447 ± 8	13 ± 6	1.63 ± 0.01
Oct 31, 2017	WP96	0.58 ± 0.13	0.17 ± 0.04	0.74 ± 0.14	553 ± 14	42 ± 4	3.89 ± 0.46
Dec 5, 2017	WP96	0.43 ± 0.15	0.42 ± 0.01	0.85 ± 0.15	549 ± 5	38 ± 2	2.76
Dec 11, 2017	WP96	0.53 ± 0.16	0.35 ± 0.01	0.88 ± 0.16	412 ± 9	32 ± 3	0.68
Jan 17, 2018	WP96	0.62 ± 0.02	0.23 ± 0.07	0.85 ± 0.07	371 ± 10	27 ± 4	0.06 ± 0.01
Feb 19, 2018	WP96	0.29 ± 0.18	0.28 ± 0.03	0.57 ± 0.18	351 ± 15	24 ± 2	0.12 ± 0.03
April 3, 2018	WP96	0.12 ± 0.06	0.26 ± 0.03	0.38 ± 0.06	527 ± 49	45 ± 9	0.58 ± 0.25
April 9, 2018	WP96	0.68 ± 0.01	0.10 ± 0.01	0.78 ± 0.01	498 ± 60	36 ± 10	0.10
May 23, 2018	WP96	0.36 ± 0.04	0.67 ± 0.18	1.03 ± 0.19	525 ± 46	47 ± 9	0.29 ± 0.18
Jul 22, 2018	WP96	0.36	0.61 ± 0.02	0.96 ± 0.02	221 ± 12	21 ± 2	0.19 ± 0.01
Aug 29, 2018	WP96	0.94 ± 0.32	1.98 ± 0.23	2.92 ± 0.23	504 ± 11	42 ± 18	0.28 ± 0.01
Sept 27, 2018	WP96	0.69 ± 0.03	1.05 ± 0.07	1.75 ± 0.07	508 ± 1	47 ± 1	0.32 ± 0.05
Oct 16, 2018	WP96	0.47 ± 0.03	0.62 ± 0.03	1.09 ± 0.03	281 ± 35	26 ± 2	0.34 ± 0.47
Dec 6, 2018	WP96	0.73 ± 0.05	0.40 ± 0.12	1.14 ± 0.12	481 ± 7	12 ± 1	2.15 ± 0.17

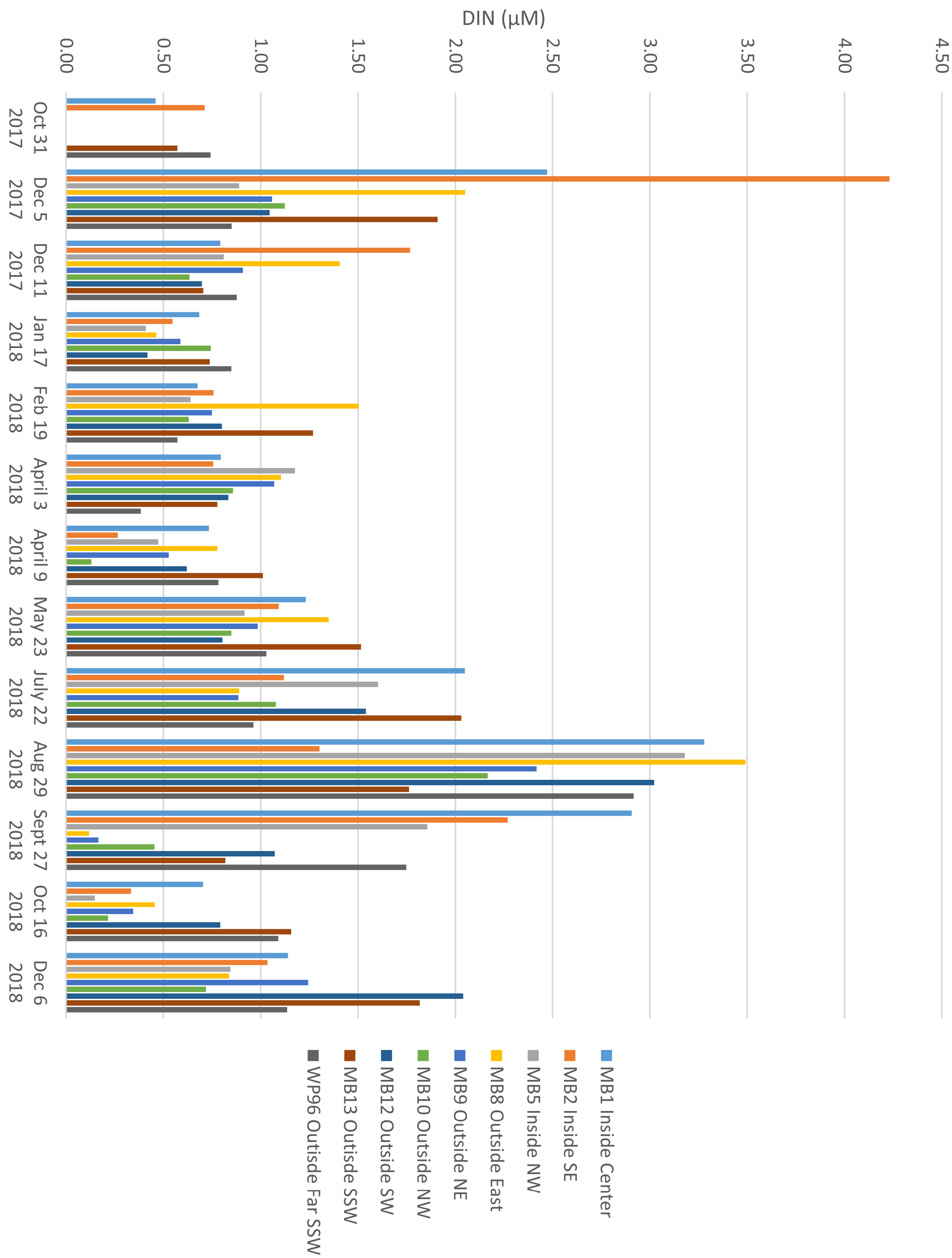
Date	Station	NOx^- (µM)	NH_4^+ (µM)	DIN (µM)	DOC (µM)	TN (µM)	Chl-a (µg/L)
Oct 31, 2017	E02	1.02 ± 0.08	0.64 ± 0.04	1.66 ± 0.09	259 ± 25	21 ± 2	0.12 ± 0.08
Dec 5, 2017	E02	0.21 ± 0.01	0.38 ± 0.04	0.59 ± 0.04	433 ± 33	32 ± 4	2.06 ± 0.35
Dec 11, 2017	E02	1.17 ± 0.57	1.44 ± 0.01	2.61 ± 0.57	400 ± 33	37 ± 13	0.44
Jan 17, 2018	E02	0.33 ± 0.15	0.22 ± 0.09	0.55 ± 0.18	340 ± 2	24 ± 1	0.12 ± 0.01
Feb 19, 2018	E02	0.22 ± 0.07	0.41 ± 0.01	0.62 ± 0.07	162 ± 5	10 ± 1	0.12 ± 0.03
April 3, 2018	E02	0.20 ± 0.06	0.13 ± 0.01	0.33 ± 0.06	182 ± 17	35 ± 11	0.08 ± 0.01
April 9, 2018	E02	0.15 ± 0.04	0.03	0.15 ± 0.04	269 ± 85	30 ± 26	0.05
May 23, 2018	E02	0.24 ± 0.09	0.16 ± 0.01	0.40 ± 0.09	394 ± 23	31 ± 4	0.19 ± 0.05
Jul 22, 2018	E02	0.22 ± 0.04	0.91 ± 0.01	1.14 ± 0.04	205 ± 13	24 ± 1	0.26 ± 0.01
Aug 29, 2018	E02	0.13 ± 0.03	1.68 ± 0.12	1.81 ± 0.12	195 ± 13	19 ± 2	0.12 ± 0.04
Sept 27, 2018	E02	0.31 ± 0.11	0.37 ± 0.07	0.68 ± 0.13	316 ± 56	31 ± 3	0.17 ± 0.04
Oct 16, 2018	E02	0.29 ± 0.30	0.21 ± 0.13	0.50 ± 0.33	117 ± 13	12 ± 3	0.11 ± 0.05
Dec 6, 2018	E02	0.49 ± 0.18	0.03 ± 0.03	0.52 ± 0.19	512 ± 18	11 ± 1	6.86 ± 0.35
Oct 31, 2017	J01	0.95 ± 0.12	0.78 ± 0.07	1.73 ± 0.14	186 ± 7	16 ± 3	0.22 ± 0.02
Dec 5, 2017	J01	0.38 ± 0.17	0.56 ± 0.20	0.94 ± 0.27	307 ± 3	25 ± 2	1.45 ± 0.08
Dec 11, 2017	J01	0.84 ± 0.34	1.44 ± 0.07	2.28 ± 0.35	363 ± 9	30 ± 3	0.35
Jan 17, 2018	J01	0.29 ± 0.08	0.44 ± 0.01	0.73 ± 0.08	314 ± 13	21 ± 3	0.13 ± 0.02
Feb 19, 2018	J01	0.09 ± 0.04	0.35 ± 0.06	0.44 ± 0.07	123 ± 2	9 ± 1	0.11 ± 0.01
April 3, 2018	J01	0.19 ± 0.03	0.41 ± 0.03	0.61 ± 0.05	176 ± 10	41 ± 16	0.07 ± 0.02
April 9, 2018	J01	0.58 ± 0.08	0.35 ± 0.02	0.92 ± 0.08	229 ± 38	35 ± 21	0.08
May 23, 2018	J01	0.28 ± 0.04	0.75 ± 0.04	1.03 ± 0.06	230 ± 46	17 ± 2	0.10 ± 0.03
Jul 22, 2018	J01	0.32 ± 0.03	2.03 ± 0.09	2.36 ± 0.09	241 ± 10	26 ± 5	0.29 ± 0.01
Aug 29, 2018	J01	0.74 ± 0.18	1.27 ± 0.41	2.01 ± 0.41	172 ± 28	16 ± 5	0.16 ± 0.04
Sept 27, 2018	J01	0.26 ± 0.14	0.72 ± 0.02	0.99 ± 0.02	420 ± 47	38 ± 2	0.18 ± 0.01
Oct 16, 2018	J01	0.34 ± 0.10	0.50 ± 0.07	0.84 ± 0.07	146 ± 15	16 ± 6	0.18 ± 0.02
Dec 6, 2018	J01	0.24 ± 0.06	0.06 ± 0.02	0.30 ± 0.02	551 ± 32	13 ± 2	7.53 ± 0.51
Oct 31, 2017	BP	1.60 ± 0.31	1.59 ± 0.25	3.20 ± 0.40	168 ± 9	19 ± 3	0.30 ± 0.12
Dec 5, 2017	BP	0.71 ± 0.32	0.37 ± 0.02	1.09 ± 0.32	314 ± 15	27 ± 5	1.78 ± 0.56
Dec 11, 2017	BP	ND	ND	ND	ND	ND	ND
Jan 17, 2018	BP	0.22 ± 0.06	0.27 ± 0.01	0.49 ± 0.07	213 ± 59	20 ± 6	0.11 ± 0.04
Feb 19, 2018	BP	0.39 ± 0.03	0.47 ± 0.02	0.87 ± 0.03	159 ± 8	9 ± 2	0.11 ± 0.01
April 3, 2018	BP	0.43 ± 0.24	0.31 ± 0.01	0.74 ± 0.24	219 ± 28	37 ± 9	0.05 ± 0.01
April 9, 2018	BP	0.60 ± 0.28	0.24 ± 0.01	0.84 ± 0.28	229 ± 2	24 ± 2	0.06 ± 0.02
May 23, 2018	BP	0.22 ± 0.06	0.06 ± 0.01	0.28 ± 0.06	251 ± 40	19 ± 4	0.38
June 25, 2018	BP	0.36 ± 0.29	0.72 ± 0.02	1.08 ± 0.29	287 ± 6	20 ± 1	0.21
June 26, 2018	BP	0.37 ± 0.08	1.38 ± 0.04	1.75 ± 0.09	302 ± 12	37 ± 11	0.06
Jul 22, 2018	BP	0.20 ± 0.10	1.32 ± 0.11	1.52 ± 0.15	299 ± 7	29 ± 2	0.32 ± 0.11
Aug 29, 2018	BP	1.22 ± 0.48	1.09 ± 0.12	2.31 ± 0.49	250 ± 18	25 ± 5	0.21 ± 0.01
Sept 5, 2018	BP	1.60 ± 0.65	0.96 ± 0.60	2.55 ± 0.88	150 ± 18	16 ± 6	0.71 ± 0.07
Sept 27, 2018	BP	0.53 ± 0.10	0.35 ± 0.01	0.89 ± 0.10	230 ± 10	26 ± 4	0.12 ± 0.03
Oct 16, 2018	BP	0.43 ± 0.14	0.14 ± 0.07	0.58 ± 0.15	147 ± 7	16 ± 5	0.10 ± 0.00
Dec 6, 2018	BP	0.22 ± 0.05	0.30 ± 0.03	0.52 ± 0.06	252 ± 5	5 ± 1	0.40 ± 0.08

APPENDIX 2: GPS COORDINATES FOR COLLECTION STATIONS

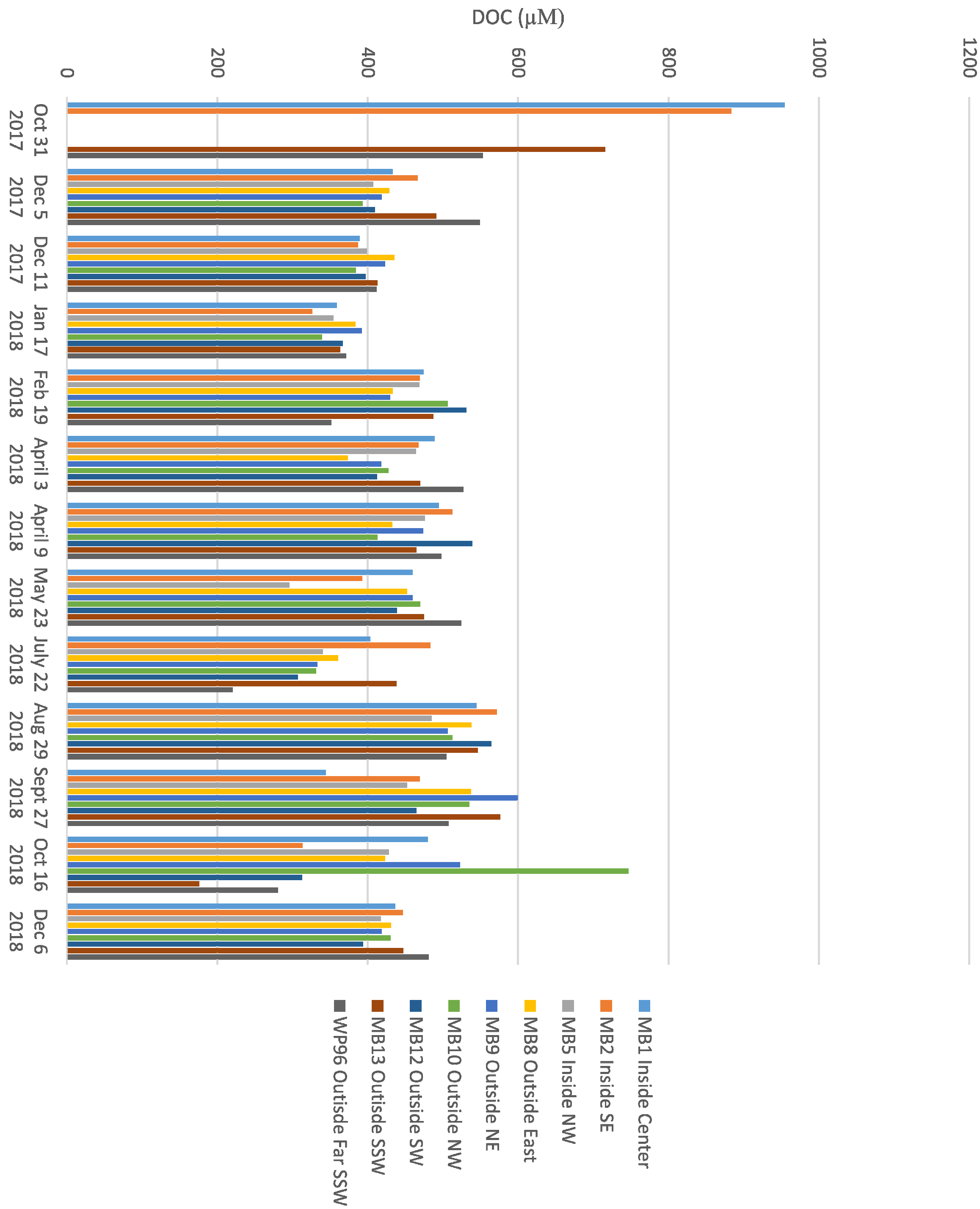
Field Sites:

- MB 1: (24°56'30.42"N, 80°49'31.80"W)
- MB 2: (24°56'13.48"N, 80°49'24.73"W)
- MB 5: (24°56'51.01"N, 80°49'41.39"W)
- MB 8: (24°56'25.59"N, 80°48'16.13"W)
- MB 9: (24°57'31.98"N, 80°48'40.78"W)
- MB 10: (24°57'27.85"N, 80°49'59.96"W)
- MB 12: (24°55'33.22"N, 80°50'29.76"W)
- MB 13: (24°55'27.27"N, 80°48'51.64"W)
- WP 96: (24°54'30.36"N, 80°48'49.14"W)
- E 02: (24°50'45.32"N, 80°48'51.02"W)
- J 01: (24°49'54.30"N, 80°48'44.82"W)
- BP: (24°45'24.60"N, 80°58'55.00"W)
- Dock: (24°42'45.31"N, 81° 5'54.89"W)

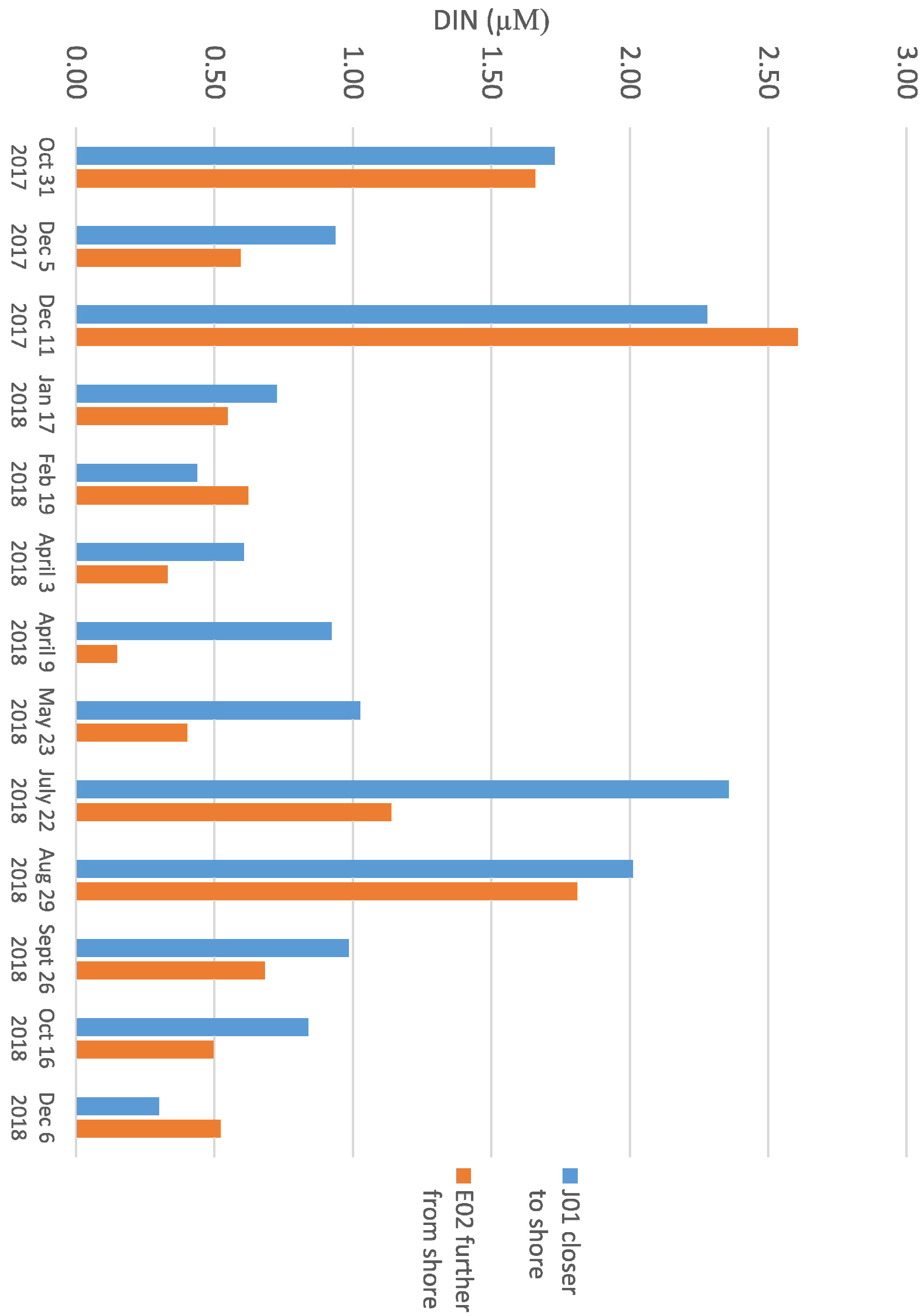
APPENDIX 3: FIGURES OF STATIONS REPRESENTING SITES



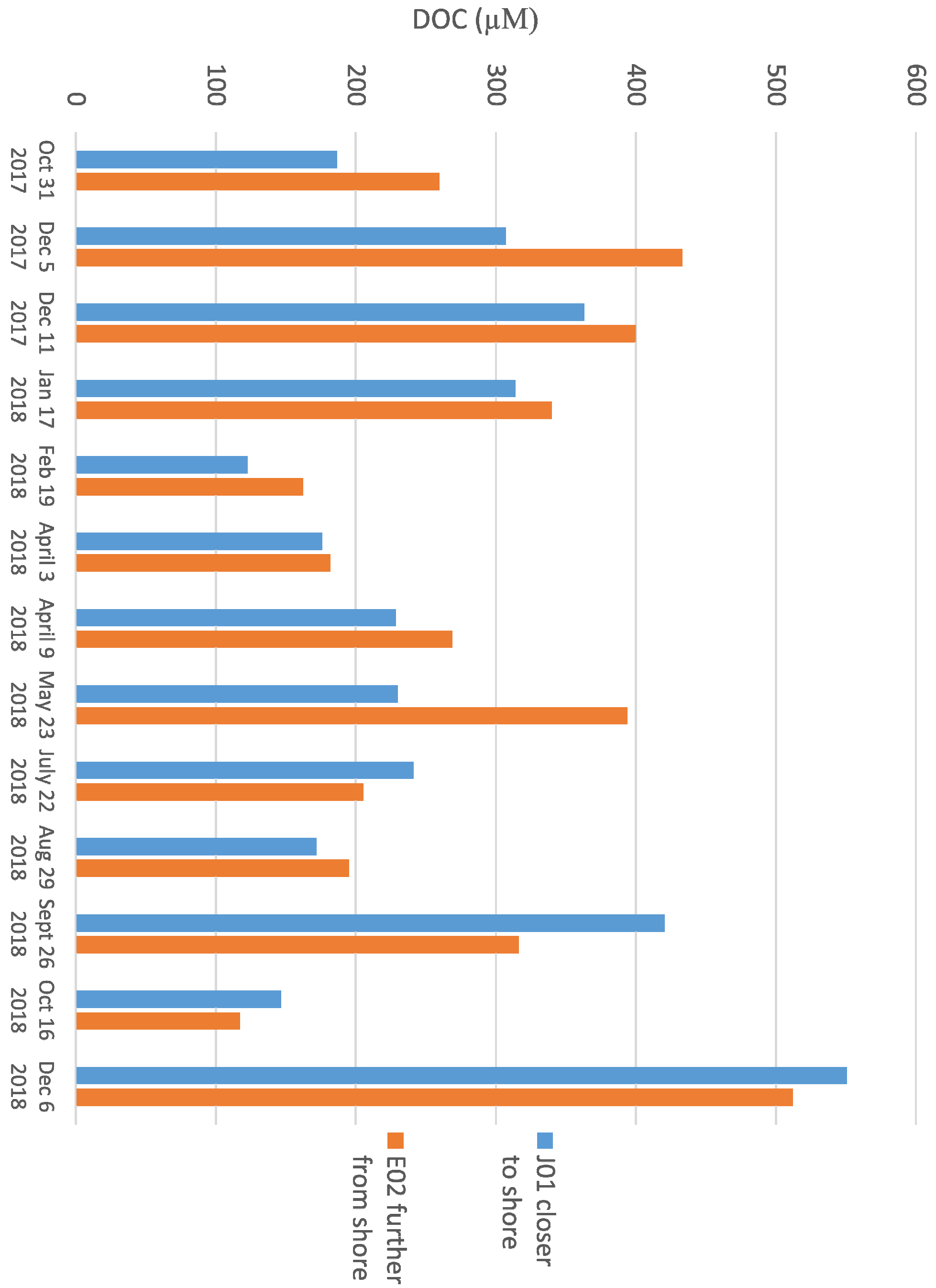
A3.1: DIN Concentrations Across MB Stations.



A3.2: DOC Concentrations Across MB Stations.

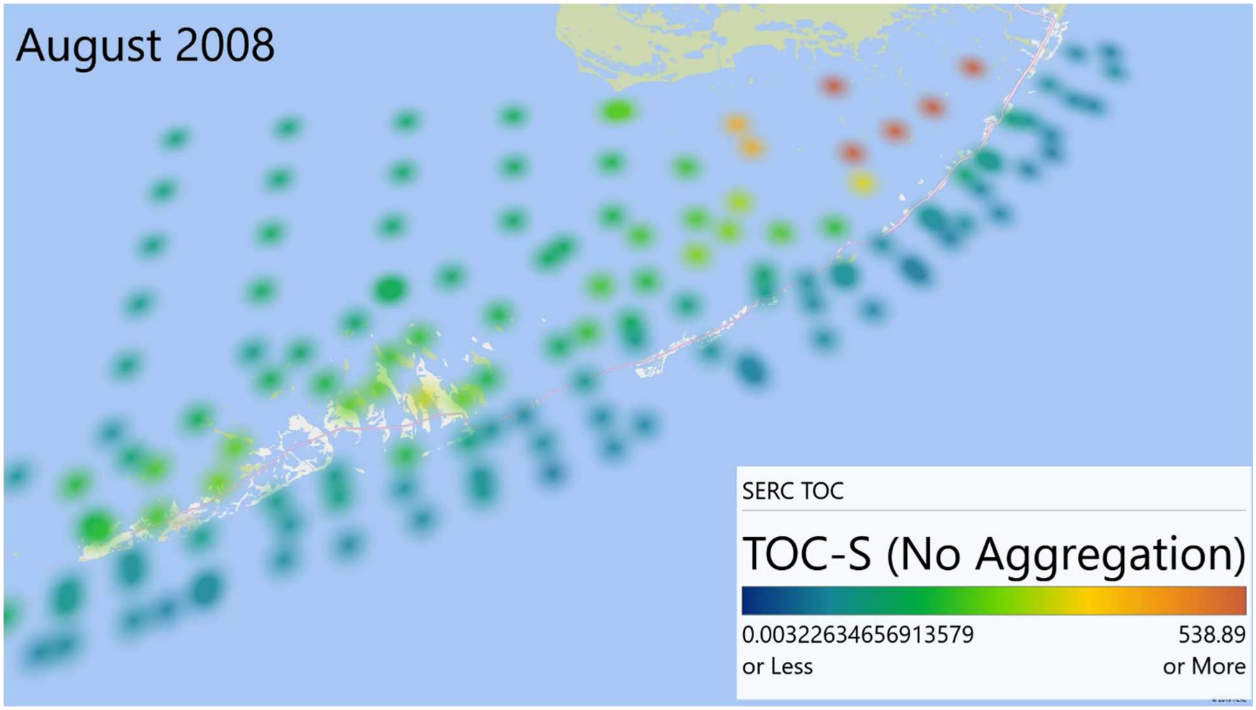


A3.3: DIN Concentrations Across Long Key Stations.



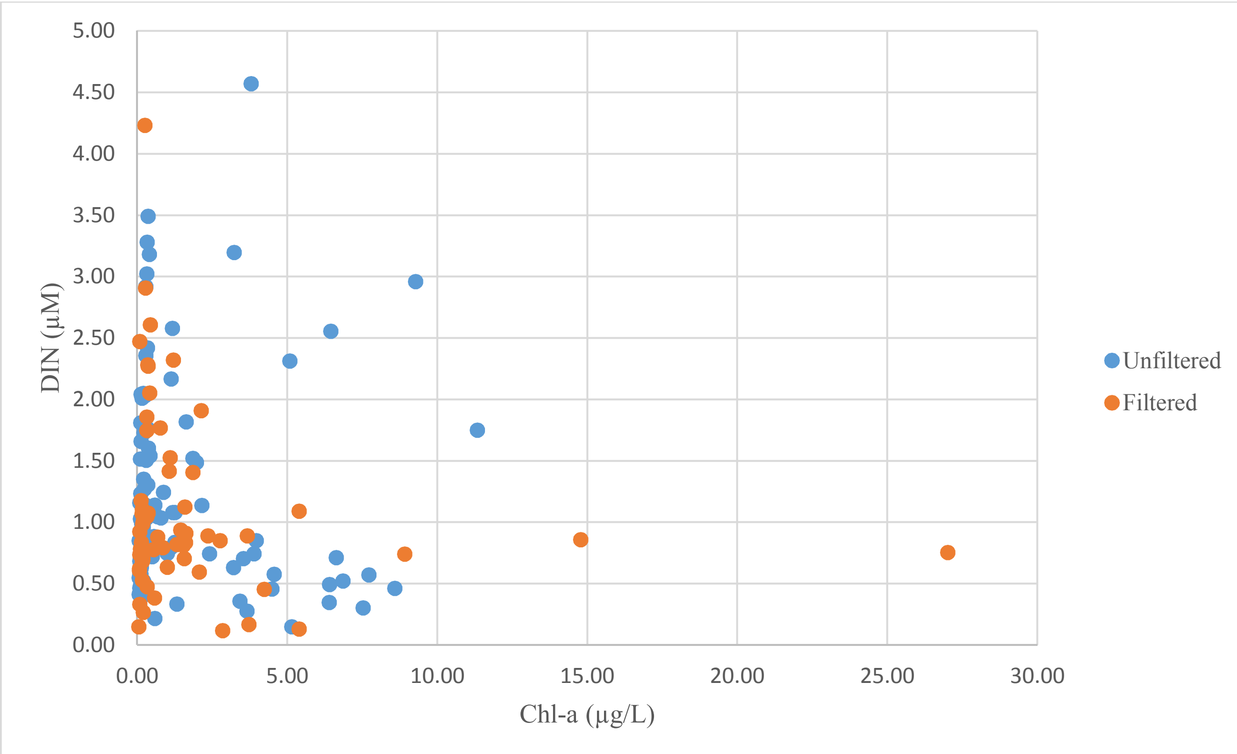
A3.4: DOC Concentrations Across Long Key Stations.

APPENDIX 4: SERC TOC DATA

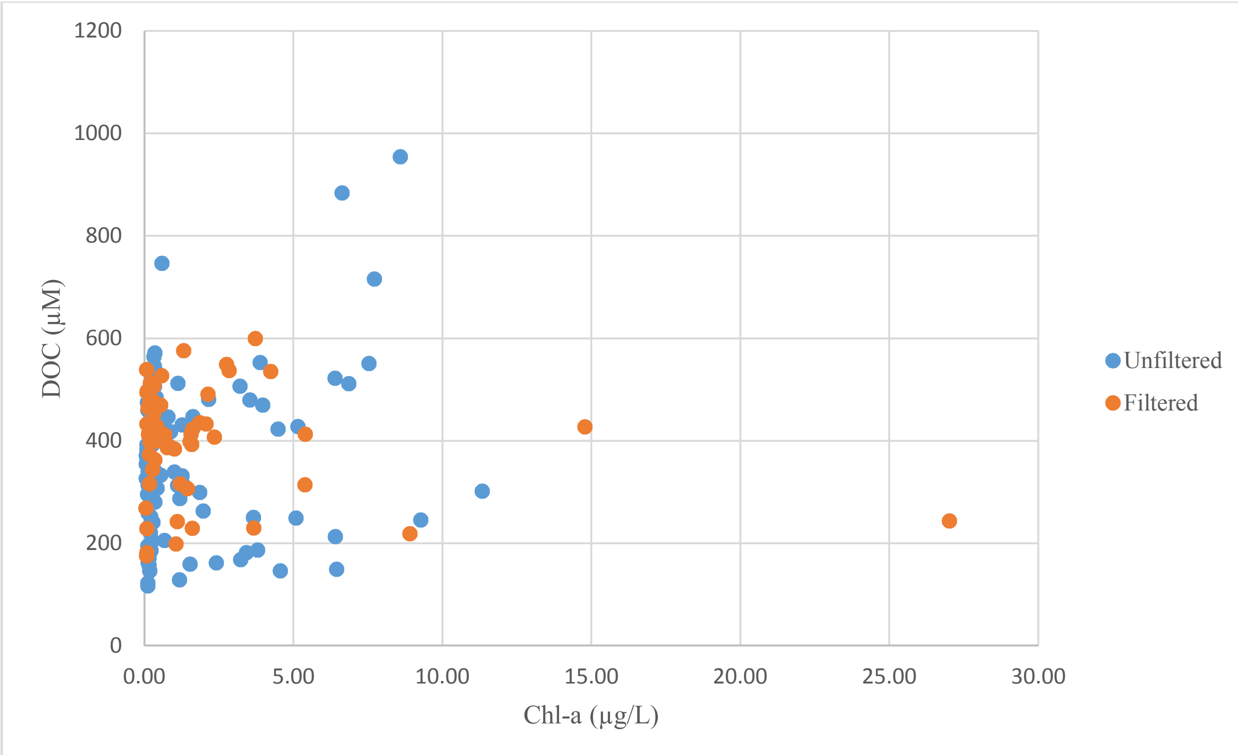


This graphic map displays the Total Organic Carbon (TOC) at a multitude of sites from the SERC data set on August 2008. The concentration of TOC [µM] increases with proximity to the Everglades in the main section of Florida Bay, with some increases in further down the keys. This relates to the theory proposed in the study about a source closer to the MB stations compared to our nearshore sites.

APPENDIX 5: FILTERED AND UNFILTERED COMPARISON



A5.1: DIN and Chlorophyll-a Comparisons. The data in this figure does not show statistical significance between the unfiltered and filtered samples prior to sampling in regards to DIN concentrations as a function of Chl-a measurements. Results based on 107 unfiltered samples prior to freezing and 63 filtered samples prior to freezing.



A5.2: DOC and Chlorophyll-a Comparisons. The data in this figure does not show statistical significance between the unfiltered and filtered samples prior to sampling in regards to DOC concentrations as a function of Chl-a measurements. Results based on 107 unfiltered samples prior to freezing and 63 filtered samples prior to freezing.

REFERENCES

Adornato, L., R., E. A. Kaltenbacher, T. A. Villareal, and R. H. Byrne. 2005. Continuous in situ determinations of nitrite at nanomolar concentrations. *Deep-Sea Res.* 52: 543–551.

Adornato, L., E. A. Kaltenbacher, D. R. Greenhow, and R. H. Byrne. 2007. High-resolution *in situ* analysis of nitrate and phosphate in the oligotrophic ocean. *Environ. Sci. Technol.* 41: 4045-4052.

Blaedel, W. J., V. W. Meloche, J. A. Ramsay. 1951. A comparison of criteria for the rejection of measurements. *J. Chem. Ecol.* 28: 643-647.

Bollinger, M. A., K. E. Maxwell, and W. C. Sharp. 2018. Documenting the effects of Hurricane Irma on staghorn coral (Acropora cerviconis) restoration sites and a near-shore sponge community in the Florida Keys. Benthic Ecology Meeting. Corpus Christi, TX. Poster.

Bosence, D. 1989. Biogenic Carbonate Production in Florida Bay. *B. Mar. Sci.* 44: 419-433.

Boyer, J. N., J. W. Fourqurean, and R. D. Jones. 1997. Spatial characterization of water quality in Florida Bay and Whitewater Bay by multivariate analyses: zones of similar influence. *Estuaries*. 20: 743-758.

Boyer, J. N., J. W. Fourqurean, and R. D. Jones. 1999. Seasonal and long-term trends in the water quality of Florida bay (1989-1997). *Estuaries*. 22: 417–430.

Boyer, J. N., C. R. Kelble, P. B. Ortner, and D. T. Rudnick. 2009. Phytoplankton bloom status: chlorophyll a biomass as an indicator of water quality condition in the southern estuaries of Florida, USA. *Ecol. Indic.* 9: S56-S67.

Briceño, H. O. and J. N. Boyer. 2010. Climatic controls on phytoplankton biomass in a sub-tropical estuary, Florida Bay, USA. *Estuar. Coast.* 33: 541-553.

Briceño, H. O., J. N. Boyer, J. Castro, and P. Harlem. 2013. Biogeochemical classification of South Florida's estuarine and coastal waters. *Mar. Pollut. Bull.* 75: 187-204.

Butler, M. J., J. H. Hunt, W. F. Herrnkind, D. L. Childress, R. Bertelsen, W. Sharp, T. Matthews, J. Field, and H. G. Marshall. 1995. Cascading disturbances in Florida Bay, USA: cyanobacteria blooms, sponge mortality, and implications for juvenile spiny lobsters *Panulirus argus*. *Mar. Ecol. Prog. Ser*. 129: 119–125.

Capone, D. G., S. E. Dunham, S. G. Horrigan, and L. E. Duguay. 1992. Microbial nitrogen transformations in unconsolidated coral reef sediments. *Mar. Ecol. Prog. Ser.* 80: 75–88.

Corredor, J. E., C. R. Wilkinson, V. P. Vicente, J. M. Morell, and E. Oetero. 1988. Nitrate release by Caribbean reef sponges. *Limnol. Oceanogr.* 33: 114-120.

Durako, M. J., M.O. Hall,and M. Merello. 2002. Patterns of change in the seagrass dominated Florida Bay hydroscape. Pp. 523–537 in J. W. Porter and K.G. Porter, eds. The Everglades, Florida Bay, and Coral Reefs of the Florida Keys: An Ecosystem Sourcebook. CRC Press, Boca Raton, Florida.

Fourqurean, J. W., J. C. Zieman, and G. V. N. Powell. 1992. Relationships between porewater nutrients and seagrasses in a subtropical carbonate environment. *Mar. Biol.* 114: 57-65.

Fourqurean, J. W., R. Jones, and J. Zieman. 1993. Processes influencing water column nutrient characteristics and phosphorus limitation of phytoplankton biomass in Florida Bay, FL, USA: inferences from spatial distributions. *Estuar. Coast. Shelf. S.* 36: 295–314.

Fourqurean, J. W., M. B. Robblee. 1999. Florida Bay: A history of recent ecological changes. *Estuaries* 22: 345–357.

Hall, M. O., M. J. Durako, J. W. Fourqurean, and J. C. Zieman. 1999. Decadal changes in seagrass distribution and abundance in Florida Bay. *Estuaries*. 22: 445-459.

Hentschel, U., K. M. Usher, M. W. Taylor. 2006. Marine sponges as microbial fermenters. *FEMS Microbiol. Ecology* 55: 167-177.

Hitchcock, G. E., E. J. Philips, L. Brand, D. Morrison. 2007. Plankton Blooms. In: Hunt, J. H., and W. Nuttle, eds. 2007. Florida Bay science program: a synthesis of research on Florida Bay. Fish and Wildlife Research Institute Technical Report TR-11.

Hoer, D. (2015). The role of marine sponges in carbon and nitrogen cycles of coral reef and nearshore environments. UNC, 2015 Carolina Digital Repository.

Hoer, D., J. Tommerdahl, N. Lindquist, and C. Martens. 2018. Dissolved inorganic nitrogen fluxes from common Florida Bay (USA) sponges. *Limnol. Oceanogr.* doi: 10.1002/lno.10960

Holmes, R. M., A. Aminot, R. Kérouel, B. A. Hooker, and B. J. Peterson. 1999. A simple and precise method for measuring ammonium in marine and freshwater ecosystems. *Can. J. Fish. Aquat. Sci.* 56: 1801–1808.

Hunt, J. H., and W. Nuttle, eds. 2007. Florida Bay science program: a synthesis of research on Florida Bay. Fish and Wildlife Research Institute Technical Report TR-11.

Jiménez, E., and M. Ribes. 2007. Sponges as a source of dissolved inorganic nitrogen: Nitrification mediated by temperate sponges. *Limnol. Oceanogr.* 52: 948-958.

Lapointe, B. E., and P. J. Barile. 2004. Comment on J. C. Zieman, J. W. Fourqurean, and T. A. Frankovich. 1999. Seagrass Die-off in Florida Bay: Long-term Trends in Abundance and Growth of Turtle Grass, *Thalassia testudinum. Estuaies* 22:460-470. *Estuaries.* 27: 157-178.

Lindell, D., S. Penno, M. Al-Qutob, E. David, T. Rivlin, B. Lazar, and A. F. Post. 2005. Expression of the nitrogen stress response gene ntcA reveals nitrogen sufficient Synechococcus populations in the oligotrophic northern Red Sea. *Limnol. Oceanogr.* 50: 1932–1944.

Nuttle, W. K., J. W. Fourqurean, B. J. Cosby, J. C. Zieman, B. Robblee, and F. Bay. 2000. Influence of net freshwater supply on salinity in Florida Bay. *Water Resour. Res.* 36: 1805–1822.

Paerl, H. W., J. R. Crosswell, B. Van Dam, N. S. Hall, K. L. Rossignol, C. L. Osburn, A. G. Hounshell, R. S. Sloup, L. W. Harding Jr. Two decades of tropical cyclone impacts on North Carolina's estuarine carbon, nutrient and phytoplankton dynamics: implications for biogeochemical cycling and water quality in a stormier world. *Biogeochemistry.* 141: 307-332.

Prager, E. J., and R. B. Halley. 1997. Florida Bay Bottom Types. Open File Report. *U.S. Geological Survery Publication.* doi: 10.3133/ofr97526

Peterson, B. J., C. D. Rose, L. M. Rutten, and J. W. Fourqurean. 2002. Disturbance and recovery following catastrophic grazing: studies of a successional chronosequence in a seagrass bed. *Oikos* 97: 361–370.

Peterson, B. J., C. M. Chester, F. J. Jochem, J. W. Fourqurean. 2006. Potential role of sponge communities in controlling phytoplankton blooms in Florida Bay. *Mar. Ecol. Prog. Ser.* 328: 93-103.

Phlips, E. J., S. Badylak, and T. C. Lynch. 1999. Blooms of the picoplanktonic cyanobacterium Synechococcus in Florida Bay, a subtropical inner-shelf lagoon. *Limnol. Oceanogr.* 44: 1166–1175.

Rok, A. and C. S. Martens. (2019). An oxygen budget for Mystery Basin, Florida Bay. In Prep.

Rudnick, D. 2007. Algal Blooms in Eastern Florida Bay and Southern Biscayne Bay. Water Resources Advisory Committee, South Florida Water Management District. Presentation.

SERC-FIU WQMN Program. Data were provided by the SERC-FIU Water Quality Monitoring Network which is supported by SFWMD/SERC Cooperative Agreement #4600000352 as well as EPA Agreement #X7-96410603-3.

Southwell, M. W., B. N. Popp, and C. S. Martens. 2008a. Nitrification controls on fluxes and isotopic composition of nitrate from Florida Keys sponges. *Mar. Chem.* 108: 96-108.

Southwell, M. W., J. B. Weisz, C. S. Martens, and N. Lindquist. 2008b. In situ fluxes of dissolved inorganic nitrogen from the sponge community on Conch Reef, Key Largo, Florida. *Limnol. Oceanogr.* 53: 986–996.

Tengberg, A., E Almroth, and P. Hall. 2003. Resuspension and its effects on organic carbon recycling and nutrient exchange in coastal sediments: in situ measurements using new experimental technology. *J. Exp. Mar. Biol. Ecol.* 285-286: 119-142.

Yarbro. L.A. and P. R. Carlson. 1998. Seasonal and spatial variation of phosphorus, iron and sulfide in Florida Bay sediments. Abstract in Proceedings, 1998 Florida Bay Science Conference, Miami, Florida

Yarbro, L. A. and P. R. Carlson. 2008. Community oxygen and nutrient fluxes in seagrass beds of Florida Bay, USA. *Estuaries. Coasts.* 31: 877–897.

Yentsch, C. S. and D. W. Manzel. 1963. A method for the determination of phytoplankton chlorophyll and phaeophytin by fluorescence. *Deep-Sea Res.* 10: 221–231.

Zieman, J. C., J. W. Fourqurean, and T. A. Frankovich. 1999. Seagrass die-off in Florida Bay: long term trends in abudnace and growth of turtle grass, *Thalassia testudinum*. *Estuaries.* 22: 460-470.